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DERIVATIVES AND ATOMIC MASS OF PALLADIUM.

BY WILLETT LEPLEY HARDIN.

Received July 14, 1899.

I. DERIVATIVES OF PALLADIUM.

THE ammonium derivatives of palladium have been very thoroughly investigated, and various classes of compounds have been prepared. The pallad-diammonium compounds are probably the most important of these derivatives. The constitution of this class of compounds is usually represented by the formula

$$Pd\begin{matrix}NH_3X\\NH_3X\end{matrix},$$

where X is a univalent radical (usually chlorine, bromine, or iodine).

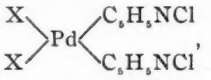
The palladium derivatives of organic bases have been investigated only to a very limited extent. In 1853 Müller[1] prepared a compound of ethylamine and palladous chloride, and suggested the formula

$$N\left\{\begin{matrix}C_4H_5\\H\\H\\Pd\end{matrix}\right\}Cl.$$

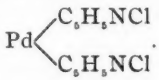
[1] *Ann. Chem.* (Liebig), **86**, 366 (1853).

He also prepared the aniline derivative of palladous chloride, and described it as a yellow crystalline compound. No analyses were made of these compounds, but Müller considered them as analogous to the pallad-diammonium derivatives.

Quite recently Rosenheim and Maass,[1] have prepared a number of derivatives of pyridine with quadrivalent palladium. These compounds are represented by the formula



where X represents chlorine, bromine, or iodine. These experimenters also prepared and analyzed the compound

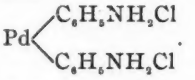


This appears to be the only derivative of bivalent palladium with an organic base, which has been analyzed. The compound was prepared by treating palladous chloride, dissolved in aqueous hydrochloric acid, with pyridine. It consists of a bright yellow crystalline powder.

In the present investigation several derivatives of bivalent palladium with organic bases have been prepared and analyzed. The compounds correspond to the pallad-diammonium salts, and are named as derivatives of these compounds.

Diphenyl-pallad-diammonium Chloride.

When a slight excess of aniline is added to a hydrochloric acid solution of palladous chloride, a voluminous yellow precipitate is formed. The compound is insoluble in hydrochloric acid, but soluble in ammonium hydroxide. When heated in a platinum spoon the substance takes fire and burns with a smoky flame. The compound is similar in appearance to the pallad-diammonium derivative, and its analysis gave results corresponding to this class of compounds. The constitution therefore may be represented by the formula



The results of the analysis are as follows :

[1] *Zischr. anorg. Chem.*, 18, 331 (1898).

	Calculated.	Found.
Palladium	29.39	29.5
Chlorine	19.47	19.32

It may be mentioned also that aniline precipitates palladium quantitatively.

Diphenyl-pallad-diammonium Bromide.

This compound was prepared in a manner similar to that of the chloride; that is, by precipitating the hydrobromic acid solution of palladous bromide with aniline. The substance is similar to the chloride in appearance. The results of the analysis, and those calculated from the formula $Pd(C_6H_5NH_2Br)_2$ are as follows:

	Calculated.	Found.
Palladium	23.62	23.8
Bromine	35.27	35.4

Dipyridine-pallad-diammonium Chloride.

The preparation and analysis of this compound correspond exactly with the work of Rosenheim and Maass. The substance is pale yellow in color, and soluble in excess of pyridine or in ammonium hydroxide. The analysis gave:

	Per cent.
Palladium	32.0
Chlorine	20.8

This corresponds to the formula

$$Pd\begin{matrix}C_5H_5NCl\\C_5H_5NCl\end{matrix}.$$

The theoretical values for palladium and chlorine from this formula are 32 and 21.1 per cent. respectively.

Diquinoline-pallad-diammonium Chloride.

When quinoline is added to a hydrochloric acid solution of palladous chloride a pale yellow precipitate is formed, which dissolves in excess of the quinoline to a colorless solution. On adding hydrochloric acid to the solution the substance is reprecipitated. The values obtained for the percentage of palladium and chlorine, and those calculated from the formula

$$Pd\begin{matrix}C_9H_7NCl\\C_9H_7NCl\end{matrix}$$

are as follows:

	Calculated.	Found.
Palladium	24.5	24.8
Chlorine	16.26	16.0

Diquinoline-pallad-diammonium Bromide.

This compound was prepared from the palladous bromide and hydrobromic acid, in a manner similar to that outlined in the preparation of the chloride. Its physical properties are similar to those of the chloride. The analysis gave 20 per cent. palladium and 30.4 per cent. bromine. The theoretical values for the formula

$$Pd\begin{cases} C_9H_7NBr \\ C_9H_7NBr \end{cases}$$

are 20.38 and 30.05 per cent. respectively.

Dipiperidine-pallad-diammonium Chloride.

On adding piperidine to a hydrochloric acid solution of palladous chloride a pale yellow precipitate is formed, which is soluble in excess of piperidine. The substance is reprecipitated by hydrochloric acid. The palladium content was found to be 31 per cent. while that calculated from the formula

$$Pd\begin{cases} C_5H_{11}NCl \\ C_5H_{11}NCl \end{cases}$$

is 30.73 per cent.

The compounds which have been described are all derivatives of pallad-diammonium compounds. Hydrogen does not attack these substances at the ordinary temperature, but when brought in contact with them in a combustion tube a very small flame is sufficient to induce the reaction. The analyses were made by reducing the compounds to metal in a current of hydrogen. The volatile products were conducted into solutions of silver nitrate where the halogen content was precipitated. In order to prevent the occlusion of hydrogen the resulting metal, in every case, was allowed to cool in a current of air.

No experiments were made with the free amines of the fatty series, but one compound was prepared by a solution of palladous chloride with ethylamine hydrochloride. When the solution was partially evaporated, brownish red scales separated. These

were dissolved in water and recrystallized. The resulting crystals were analyzed and found to contain 30.3 per cent. palladium and 40.94 per cent. chlorine. The corresponding values calculated from the formula

$$PdCl_2 2C_2H_5NH_2HCl$$

are 31.4 and 41.58 per cent. The substance is evidently a double salt corresponding to the double chloride of ammonium and palladium.

The foregoing observations, while limited to five organic bases, indicate that bivalent palladium reacts with organic amines and other bases, in a manner similar to that with ammonia.[1] The diphenyl-pallad-diammonium chloride and the corresponding bromide can be prepared with little difficulty. Both are anhydrous and insoluble in water, and can be dried at 100° without decomposition. The compounds seem to be well adapted to atomic mass determinations.

II. THE ATOMIC MASS OF PALLADIUM.

Inasmuch as the earlier determinations of the atomic mass of palladium show considerable variation, it was thought advisable to make use of some of the compounds described in part I of this paper in a redetermination of this constant. After some preliminary observations the diphenyl-pallad-diammonium chloride and the corresponding bromide were selected as being most suitable for quantitative determinations.

Historical Statement.

In 1828 Berzelius[2] made the first reliable determinations of the atomic mass of palladium. The method consisted in analyzing the double chloride of palladium and potassium. The results show considerable variation. The ratio between the palladium and the potassium chloride gave 106.22 as a mean for the atomic mass of palladium.[3]

Sixty years later Keiser[4] investigated the compound employed by Berzelius, and found that it contained "water of decrepita-

[1] Palladous chloride solutions were also precipitated with phenylhydrazine, but the compound was not analyzed.

[2] Pogg. *Ann.*, 13, 454.

[3] The atomic mass of oxygen is taken as sixteen in all the calculations in this paper.

[4] *Am. Chem. J.*, 11, 398 (1889).

tion." Keiser concluded that the potassium palladium chloride is not suitable for atomic mass determinations, and made use of pallad-diammonium chloride. The salt was carefully dried at a temperature of from 120° to 130°. The analyses were made by reducing known quantities of the substance in a current of hydrogen, and weighing the resulting metal. The mean of two series of observations gave 106.54 for the atomic mass of palladium.[1]

In 1892 Keller and Smith,[2] investigated the various methods of purifying palladium, and concluded that the method employed by Keiser does not give a product which is free from foreign metals, especially copper. These experimenters made use of an entirely different method of purification, and probably obtained purer material than any that had been employed in the earlier determinations. After obtaining the pure metal it was converted into pallad-diammonium chloride. The material was carefully dried, and the palladium content determined by the electrolysis of the ammoniacal solution in a silver-coated platinum dish. The mean of nine determinations gave 107.18 for the atomic mass of palladium. Two experiments were made by converting pallad-diammonium chloride into palladium sulphide, by means of hydrogen sulphide. The results were about two-tenths of a unit higher than those obtained by electrolysis. The weighings were not reduced to a vacuum standard.

During this same year Bailey and Lamb[3] made two series of observations on the atomic mass of palladium. They experimented with pallad-diammonium chloride, and determined both the chloine and palladium. The chlorine determinations gave 106.65, while the palladium determinations gave only 105.75 for the atomic mass of palladium. The weighings were reduced to a vacuum standard.

In 1893, Joly and Leidie[4] repeated the earlier determinations on the double chloride of potassium and palladium. The perfectly dry salt was dissolved in water acidulated with hydrochloric acid, and the solution electrolyzed. From the weight of

[1] This value is based upon Clarke's reductions to a vacuum standard.
[2] *Am. Chem. J.*, 14, 423 (1892).
[3] *J. Chem. Soc.*, 61, 745 (1892).
[4] *Compt. rend.*, 116, 147 (1893).

the metal obtained the authors gave 106.28 for the atomic mass of palladium.

During the next year Keiser and Breed[1] repeated the earlier work on the reduction of pallad-diammonium chloride. The material was carefully purified by two different methods. The mean of two series of experiments is almost identical with the value obtained by Keiser in his earlier experiments.

A glance at the foregoing results will show considerable variation. The values usually accepted for the atomic mass of palladium are as follows:

Clarke	106.36
Richards	106.5
German committee	106.0

No satisfactory explanation has yet been offered to account for these variations. Keller and Smith suggested that there may be a slight loss of material in the reduction of pallad-diammonium chloride. Keiser, however, in his second series of determinations, failed to detect any indications of such a loss. It has also been suggested that the high value obtained by Keller and Smith may have been due to the occlusion of hydrogen by the metallic palladium. Careful precautions, however, were taken to prevent any error from this source, and the authors were unable to detect the presence of hydrogen in the metallic deposit. The reliable determinations of the atomic mass of palladium are based almost entirely upon analyses of pallad-diammonium chloride. The variations then must be due either to the method of analysis or to the method of purifying the material. In the present investigation the metal was purified by the method of Keller and Smith, and the analyses were made in a manner similar to those of Keiser. The value obtained is higher than that usually accepted for the atomic mass of palladium. This would indicate that the results are influenced by the method of purifying the material.

Purification of Metallic Palladium.

As already mentioned the material used in these experiments was purified by the method outlined by Keller and Smith. The commercial metal, about twenty-five grams, was dissolved in

[1] *Am. Chem. J.*, **16**, 20 (1894).

aqua regia, and the solution evaporated to dryness on a water-bath. The residue, after evaporating several times with hydrochloric acid, was dissolved in water containing a little hydrochloric acid. The solution was diluted with water, and treated with an excess of ammonium hydroxide. Heat was applied until the palladium salt was completely dissolved. A small quantity of reddish brown material remained insoluble. This was filtered out and the filtrate treated with an excess of hydrochloric acid, when the yellow pallad-diammonium chloride was precipitated. After standing for forty-eight hours the compound was filtered out and thoroughly washed. It was then dissolved in cold, dilute ammonia water, the solution filtered, and the palladium reprecipitated as pallad-diammonium chloride.

This salt was dried and carefully ignited in the air, after which the bluish green residue was reduced in a current of hydrogen. The resulting metal was dissolved in aqua regia and the solution evaporated to dryness on a water-bath. The residue was digested with hydrochloric acid and evaporated to dryness several times. The remaining chloride was then dissolved in water containing a little hydrochloric acid, and the solution carefully neutralized with sodium carbonate. The calculated amount of mercuric cyanide was then added, and the palladium was precipitated as palladous cyanide. After standing for several days the precipitate was repeatedly washed by decantation and finally on a filter. The palladous cyanide was dried and strongly ignited for several hours in a muffle-furnace.

The metal which resulted from the ignition of the palladous cyanide was extracted with hydrochloric acid, to remove any copper oxide that might have been present, and then dissolved in aqua regia. After repeated evaporations with hydrochloric acid, a dilute solution of the palladous chloride was saturated with sulphur dioxide. The solution became yellow in color and a slight precipitate was formed on standing. Potassium thiocyanate produced a slight turbidity when added to the yellow solution. No attempt was made to determine the composition of these precipitates.[1] Upon warming, the solution lost its color.

When the sulphur dioxide had been completely removed by

[1] In the experiments of Keller and Smith these precipitates were examined and found to contain both gold and copper.

boiling, the solution was filtered, and the palladium precipitated from the neutralized filtrate by means of potassium formate. The metal came down in black flakes. The palladium thus obtained was thoroughly washed, dried, and strongly ignited for several hours in a closed porcelain crucible in a muffle-furnace. The resulting metal after treating with hydrochloric acid was heated in a current of hydrogen, when it became almost silver-white in color.

Preparation of Diphenyl-pallad-diammonium Chloride.

Pure metallic palladium, obtained in the manner just outlined, was dissolved in hydrochloric acid containing a small quantity of nitric acid. These acids had been previously purified. The resulting solution was evaporated to dryness on a water-bath. The residue was digested with hydrochloric acid and again evaporated to dryness. This was repeated until the nitric acid was completely expelled. The resulting palladous chloride was dissolved in water acidulated with hydrochloric acid. The solution after filtering was treated with a slight excess of aniline which had been purified by several redistillations.

The resulting diphenyl-pallad-diammonium chloride was allowed to stand for twelve hours in a covered beaker. It was then washed several times by decantation, and afterward washed upon a filter. The final washings were made with alcohol. The resulting material was dried for several days at the ordinary temperature, and finally dried for forty-eight hours in an air-bath at a temperature of 90°.

Method of Analysis.

The analyses were made by reducing known quantities of the substance in a current of hydrogen, and weighing the resulting metal. The material was placed in a porcelain boat which, in turn, was placed in a hard glass combustion tube. A current of pure, dry hydrogen gas was then conducted through the tube. There was no action at the ordinary temperature, but a very small flame under the tube was sufficient to induce the reaction. The temperature was gradually increased. After the reduction appeared to be complete the temperature was kept at a bright red heat for one hour. The flames were then removed, and

when the temperature had fallen below a red heat the current of hydrogen was replaced by a current of dry air. The metal was then heated to a bright red heat for a period of two hours. This precaution was taken in order to remove any carbon which might have resulted from the decomposition. It might be remarked, however, that there were no indications of free carbon in the boat. After heating in the air the metal was again heated in a current of hydrogen, and finally cooled in a current of air to prevent any occlusion of hydrogen. The resulting metal was almost silver-white in color.

In the first experiments an attempt was made to determine the quantity of chlorine by conducting the volatile products into solutions of silver nitrate. The results, however, were not accurate enough for atomic mass determinations. The values which follow are all based upon determinations of metallic palladium. The weighings were made on a short-armed Troemner balance with a set of calibrated weights. The balance is sensitive to the fortieth of a milligram. All weighings have been reduced to a vacuum standard. In order to make these reductions the density of diphenyl-pallad-diammonium chloride was determined and found to be 1.66.

First Series.

The atomic masses used in the calculation of results are those given in Clarke's report for 1898.[1] The results from seven analyses of diphenyl-pallad-diammonium chloride are as follows:

	Weight of substance. Grams.	Weight of palladium. Gram.	Atomic mass of palladium.
1	0.98480	0.28953	107.06
2	1.10000	0.32310	106.92
3	1.02820	0.30210	106.96
4	1.19230	0.35040	107.00
5	1.40550	0.41300	106.98
6	1.26000	0.37040	107.04
7	2.25510	0.66310	107.08
Mean			107.006
Maximum			107.08
Minimum			106.92
Difference			0.16

[1] This Journal, 21, 200.

Preparation of Diphenyl-pallad-diammonium Bromide.

This compound was prepared in a manner analogous to that of the chloride. The hydrobromic acid was prepared by the action of pure bromine on anthracene. The acid fumes were conducted through tubes of anthracene to remove the free bromine. It is necessary in these experiments to use hydrobromic acid which is absolutely free from bromine, for, according to Rosenheim and Maass, these compounds take up free bromine to form addition products. This precaution was carefully observed.[1] The washing and drying of the material were carried out just as in the case of the chloride. The specific gravity of the compound was found to be 1.75.

Second Series.

Five analyses of diphenyl-pallad-diammonium bromide gave the following values for the atomic mass of palladium:

	Weight of substance. Grams.	Weight of palladium. Gram.	Atomic mass of palladium.
1	0.88567	0.20917	107.01
2	1.31280	0.31000	106.99
3	1.50465	0.35540	107.03
4	2.01635	0.47635	107.05
5	2.92300	0.69080	107.10
Mean			107.036
Maximum			107.10
Minimum			106.99
Difference			0.11

Ammonium Palladium Bromide.

This salt was prepared in a pure condition by Smith and Wallace[1] as follows: Pure metallic palladium was dissolved in nitro-hydrobromic acid. The resulting solution was evaporated, and the residue repeatedly moistened with hydrobromic acid and evaporated to dryness on a water-bath. The resulting palladium bromide was dissolved in water containing a little hydrobromic acid, and to the solution was added an equivalent quantity of ammonium bromide. On evaporating the solution large olive-

[1] Before the publication of Rosenheim and Maass had been noticed, a series of experiments were made with hydrobromic acid which contained a small quantity of free bromine. The results obtained for the atomic mass of palladium were somewhat variable, and about one unit lower than those obtained from the chloride.

[2] This Journal, 16, 465 (1894).

brown crystals of ammonium palladium bromide separated. The salt was dissolved in water and recrystallized. The resulting material was carefully dried, and found to be anhydrous and stable in the air. The specific gravity of the salt is 3.40.

Third Series.

This series was made with the above salt two years ago. The results of four experiments reduced to a vacuum standard are as follows :

	Weight of substance. Grams.	Weight of palladium. Gram.	Atomic mass of palladium.
1	0.77886	0.18006	107.03
2	1.53109	0.35381	106.96
3	2.75168	0.63614	107.03
4	1.88136	0.43478	106.98
Mean			107.00
Maximum			107.03
Minimum			106.96
Difference			0.07

SUMMARY.

By combining the three series we obtain, as a mean of all the results, the following value :

First series	107.006
Second "	107.036
Third "	107.000
Mean	107.014

This value is higher than that usually accepted for the atomic mass of palladium. The earlier determinations are based almost entirely upon analyses of pallad-diammonium chloride, while in the present investigation new factors have been introduced. Both carbon and bromine are important elements of comparison in these determinations. Further investigation will probably be necessary to fully explain the variation in the results of the different experimenters. The fact, however, that the three series of results in the present work agree very closely with each other, and approximately with the value obtained by Keller and Smith, and the fact that there is no apparent source of error in the method employed, furnish a strong argument in favor of the

value 107 for the atomic mass of palladium. This value does not influence the position of palladium in the periodic system.

In conclusion I desire to express my obligations to Professor Edgar F. Smith for suggesting this line of work, and for many valuable suggestions during its prosecution.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

THE ACTION OF SODIUM METHYLATE UPON DIBROMIDES OF PROPENYL-COMPOUNDS AND OF UNSATURATED KETONES.

BY F. J. POND, O. P. MAXWELL, AND G. M. NORMAN.

Received July 28, 1899.

IT was stated in a previous paper[1] that certain phenol ethers, which contain a C_3H_5 group having the propenyl structure, give bromine addition products which, on treatment with sodium alcoholate, yield ketones of the general formula,

$$R—CO—CH_2—CH_3.$$

Thus, the dibromides of anethol,[2] methyl-,[3] ethyl-,[2] and benzyl-[1] isoeugenol and isosafrol[2] form ketones when they are treated with sodium alcoholate. As the bromine derivatives of the corresponding isomeric compounds containing the allyl group are not converted into ketones by a similar treatment, this reaction is characteristic for those compounds containing the propenyl group. Therefore, the structure of the unsaturated group, C_3H_5, in these two classes of compounds may be readily determined by means of this reaction.

The study of this reaction is here extended to isoapiol and propyl isoeugenol, both of which contain the propenyl group, $R—CH=CH—CH_3$, and form dibromides which are readily converted into ketones; the corresponding bromine derivatives of apiol and propyl eugenol do not yield ketones when subjected to an analogous treatment.

It is also shown that the dibromides of certain unsaturated ketones represented by the formula, $R—CH=CH—CO—C_6H_5$, may be readily changed into 1,3-diketones, $R—CO—CH_2—CO—C_6H_5$. The reaction by which these diketones are formed

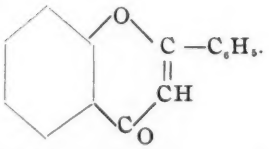
[1] Pond and Beers: This Journal, 19, 825.
[2] Wallach and Pond: *Ber. d. chem. Ges.*, **28**, 2714.
[3] Hell and Portmann: *Ibid.*, **28**, 2088; Hell and Hollenberg: *Ibid.*, **29**, 682.

seems to proceed in much the same manner as in the formation of ketones from propenyl compounds; and there appears to be reasonable ground for the belief that this method of preparing the aromatic β-diketones will prove of certain interest, and perhaps of some value in the study of this interesting class of compounds.

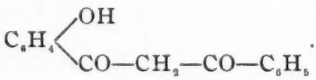
It should be noted in this connection that St. v. Kostanecki in his extended work on the unsaturated ketones obtained flavone and derivatives of flavone by the action of alcoholic potash on the dibromides of certain unsaturated *o*-oxyketones. Thus Feuerstein and St. v. Kostanecki[1] found that alcoholic potash converted 2′-acetyl oxybenzylidine acetophenone dibromide,

$$CH_3CO.O.C_6H_4—CO—CHBr—CHBr—C_6H_5,$$

into *flavone*,

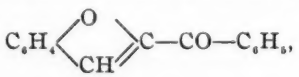


On boiling flavone with a concentrated solution of potassium hydroxide or with sodium alcoholate, it was decomposed into acetophenone, *o*-oxyacetophenone, salicylic acid and benzoic acid, indicating that the first intermediary product of decomposition was the 1,3-diketone, *o-oxybenzoylacetophenone*,



This diketone, however, could not be separated, nor was its presence noted in the formation of flavone from the dibromide of the unsaturated ketone.

Kostanecki and Tambor[2] obtained α-cumarylphenyl ketone,



by the action of warm, concentrated alcoholic potash on acetyl-2-oxybenzylidene acetophenone dibromide,

[1] Feuerstein and St. v. Kostanecki: *Ber. d. chem. Ges.*, **31**, 1760.
[2] Kostanecki and Tambor: *Ibid.*, **29**, 237.

$$C_6H_4\begin{cases}OH\\ CHBr—CHBr—CO—C_6H_5\end{cases}$$

α-Cumarylphenyl ketone decomposes into benzoic acid and cumarone when fused with potash.

These results are therefore quite distinct from those described in this paper.

EXPERIMENTAL.

The apiol,[1] $C_{12}H_{14}O_4$, used in our experiments was a very pure specimen, obtained from Schimmel & Co., of Leipzig. It was in the form of fine, white needles, which melted sharply at 30° to 31° and boiled at 294° to 295°.

Isoapiol,[2] $C_6H\begin{cases}—OCH_3\\ —OCH_3\\ —O\\ —O\end{cases}>CH_2$ $\\ —CH=CH—CH_3$.—This substance was readily prepared from apiol according to the method of Eykman,[3] and Ciamician and Silber[2] by heating apiol with an alcoholic potash solution.

Twenty-four grams of apiol were heated with a solution of fifty grams of potassium hydroxide in 250 cc. of alcohol, on a water-bath, for twenty-four hours. The resulting isoapiol was precipitated with a large quantity of water and recrystallized from alcohol. It was obtained in large, white crystals, which melted at 55° to 56°.

Isoapiol Dibromide, $C_6H\begin{cases}—OCH_3\\ —OCH_3\\ —O\\ —O\end{cases}>CH_2$ $\\ —CHBr—CHBr—CH$.—This compound was prepared by Ciamician and Silber[4] by adding the theoretical quantity of bromine to a solution of isoapiol in ether, which was cooled to —18°.

Twenty-nine grams (one molecule) of bromine were added

[1] Blanchet and Sell: *Ann. Chem.* (Liebig), **6**, 301; Ciamician and Silber: *Ber. d. chem. Ges.*, **21**, 913; Gerichten: *Ibid.*, **9**, 1477.

[2] Ciamician and Silber: *Ber. d. chem. Ges.*, **21**, 1621; Ginsberg: *Ibid.*, **21**, 1192; Gerichten: *Ibid.*, **9**, 1479.

[3] Eykman: *Ibid.*, **23**, 855.

[4] Ciamician and Silber: *Ibid.*, **23**, 2287.

carefully to a solution of forty grams of isoapiol in 200 cc. of dry ether, well cooled by a mixture of ice and salt. The very slight excess of bromine was at once removed by shaking with sulphurous acid, and, after evaporation of the ether, the resultant oil was dried over sulphuric acid. After standing for about twelve hours the oil solidified to a mass of small, white crystals, which were pressed on a porous plate and crystallized from petroleum ether. It melted at 70° to 72°. It is impossible to obtain this dibromide in a solid form unless the bromine be added very slowly to the ethereal solution of isoapiol, and the resulting, thick oil be carefully dried over sulphuric acid or calcium chloride in a desiccator. It decomposes at once on warming with alcohol, and tends to decompose when crystallized from ordinary solvents, petroleum ether being best adapted for its purification.

Treatment of Isoapiol Dibromide with Sodium Methylate.—Forty-three grams of isoapiol dibromide were added to a solution of ten grams of sodium in 150 cc. of methyl alcohol. A vigorous reaction took place at once with separation of sodium bromide. The reaction was completed by heating the mixture in a flask with a reflux condenser, on a water-bath, for five hours. Water was added to dissolve the sodium bromide, and the solution was acidified with hydrochloric acid, and boiled for two hours to insure the hydrolysis of the unsaturated ether, $R—C(OCH_3)=CH—CH_3$, which is formed by the action of sodium methylate on the dibromide.[1] The dark-red oil which had separated was non-volatile with steam; it was separated by a funnel and allowed to stand for twenty-four hours. At the end of this time, the oil had for the most part solidified; the crystals were filtered by the aid of the pump, and washed with cold ether in which the red oil was very easily soluble, while the crystals were only sparingly soluble. The compound was recrystallized from alcohol, and obtained in white prisms, melting at 95°.

Ketone, $C_6H\begin{matrix}—OCH_3\\—OCH_3\\—O\\—O\\—CO—CH_2—CH_3\end{matrix}>CH_2$.—It was expected that the above-mentioned solid, melting at 95°, would prove to be a ketone, since the method of its preparation was analogous to that

[1] Pond and Beers: This Journal, 19, 827.

employed in the preparation of ketones from anethol, isosafrol, etc. The substance was, indeed, readily converted into an oxime, and the latter, in turn, reverted into the ketone by warming with dilute sulphuric acid. This process gave a very pure product which crystallized from alcohol in large, white prisms, melting at 95.5°.

It was found rather difficult to remove a slight red color from the crude ketone unless the oxime was first prepared. This red color is due to a slight admixture of the red oil which is formed together with the ketone.

The pure crystals gave the following results on combustion:

I. 0.1366 gram gave 0.3045 gram carbon dioxide and 0.0692 gram water.

II. 0.1242 gram gave 0.2760 gram carbon dioxide and 0.0664 gram water.

	Calculated for $C_6H(OCH_3)_2O>CH_2$ $-CO-CH_2-CH_3$	Found. I.	II.
Carbon	60.79	60.50	60.60
Hydrogen	5.88	5.66	5.94

Oxime, $C_6H(OCH_3)_2O>CH_2$ $-C(NOH)-CH_2-CH_3$.—This compound was very easily prepared by treating six grams of the ketone with an alcoholic solution of hydroxylamine in the usual manner. It crystallizes from methyl alcohol in white needles, which melt at 124°. It is readily changed into the ketone by heating with dilute sulphuric acid on the water-bath for twenty minutes.

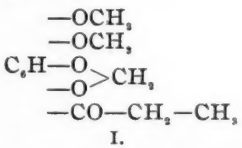
An analysis gave the following results:

I. 0.1513 gram gave 0.3142 gram carbon dioxide and 0.0786 gram water.

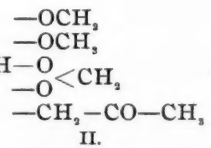
II. 0.1420 gram gave 0.2945 gram carbon dioxide and 0.0725 gram water.

	Calculated for $C_6H(OCH_3)_2O>CH_2$ $-C(NOH)-CH_2-CH_3$	Found. I.	II.
Carbon	56.91	56.63	56.56
Hydrogen	5.93	5.77	5.67

Only two formulas are possible for the ketone obtained from isoapiol; *viz.*,



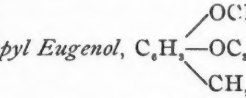
I.



II.

In order to determine between these two formulas, five grams of the oxime were dissolved in ten cc. of concentrated sulphuric acid and cautiously heated to 250°. The reaction product was diluted with water and distilled with steam. An acid having the odor of a lower fatty acid was obtained in the distillate, separated by the usual method and characterized as propionic acid. This indicates that the ketone has the structure represented by formula I, since a ketone having the formula II could not yield propionic acid by this treatment.

The ketone was reduced in an absolute alcohol solution with sodium, yielding a solid substance; this separated from ether in crystals, which melted sharply at 88° to 89°. It is probably the *alcohol*, $C_{12}H_{16}O_3$, but owing to lack of material no further work could be done with the compound.

Propyl Eugenol,  .—This compound was prepared according to the method of Cahours[1] and Wassermann[2] by heating an alcoholic solution of the potassium salt of eugenol with propyl bromide.

Fifty-seven grams of propyl bromide were added slowly to a hot solution of seventy-five grams of freshly distilled eugenol and twenty-seven grams of potassium hydroxide in 100 cc. of alcohol, and the mixture was heated for two hours on the water-bath. The reaction product was diluted with water and the resultant oil, being non-volatile with steam, was extracted with ether. The ethereal solution was dried with calcium chloride, the ether distilled off, and the propyl eugenol rectified under atmospheric pressure. On redistillation a colorless oil was

[1] Cahours: *Jsb. d. Chem.* (1877), 580; *Ber. d. chem. Ges.*, 10, 237.

[2] Wassermann: *Ann. Chem.* (Liebig), 179, 375.

obtained, which boiled at 270.5°; its specific gravity at 15° was 1.0032. Cahours[1] described this substance as a yellow oil, boiling at 263°–265°.

Propyl Isoeugenol, $C_6H_3\begin{cases}OCH_3\\OC_3H_7\\CH=CH-CH_3\end{cases}$.—This ether of isoeugenol containing the propenyl group was produced by heating an alcoholic solution of propyl eugenol with potassium hydroxide. Fifty grams of propyl eugenol, 125 grams of potassium hydroxide, and 250 cc. of alcohol, were heated in the water-bath for twenty-four hours. The reaction-mixture was poured into a large quantity of water, and the resulting solid was filtered, dried, and distilled at the ordinary pressure. It boiled without decomposition at 280°–281°. The distillate was crystallized from alcohol, and obtained in very large, beautiful, white prisms, which melted at 53°–54°.

This compound was also readily formed from isoeugenol by heating the potassium salt of the latter in an alcoholic solution with propyl bromide.

Analysis gave the following:

I. 0.1498 gram gave 0.4145 gram carbon dioxide and 0.1170 gram water.

II. 0.1422 gram gave 0.3896 gram carbon dioxide and 0.1098 gram water.

	Calculated for $C_{12}H_{18}O_2$.	Found. I.	Found. II.
Carbon	75.72	75.46	75.48
Hydrogen	8.73	8.67	8.57

Propyl Isoeugenol Dibromide, $C_6H_3\begin{cases}OCH_3\\OC_3H_7\\CHBr-CHBr-CH_3\end{cases}$.—The dibromide was quantitatively formed by adding the theoretical quantity of bromine to the well-cooled, ethereal solution of propyl isoeugenol. A very slight excess of bromine was removed by agitation with a sulphurous acid solution and the ether allowed to evaporate. No evolution of hydrobromic acid was noticed either during the addition of bromine or on evaporation of the ether. The compound at first formed an oil which

[1] Cahours: *Ber. d. chem. Ges.*, 10, 237.

gradually solidified to a mass of fine, white crystals, melting at 53°–54°. It is very soluble in alcohol and ether, but cannot be recrystallized without decomposing.

Ketone, $C_6H_3\begin{cases}OCH_3\\OC_3H_7\\CO-CH_2-CH_3\end{cases}$.—Forty-four grams of the dibromide were added to a solution of eight grams of sodium in 150 cc. of methyl alcohol, and heated on the water-bath for four hours. Water was added, an oil being thrown out, and the mixture was rendered acid with hydrochloric acid and boiled for two hours. On cooling, the oil completely solidified, and was separated, dried, and crystallized from alcohol. It is best obtained in a pure condition by distillation in a vacuum and recrystallization from methyl alcohol. It forms large, splendid prisms, which melt at 63°–64° and boil with slight decomposition at 284°–287° under atmospheric pressure. The yield of the ketone from propyl isoeugenol dibromide is quantitative.

The following are the results of the analysis:

I. 0.1316 gram gave 0.3400 gram carbon dioxide and 0.0998 gram water.

II. 0.1303 gram gave 0.3362 gram carbon dioxide and 0.0990 gram water.

	Calculated for $C_{13}H_{18}O_3$.	Found. I.	II.
Carbon	70.27	70.46	70.37
Hydrogen	8.10	8.42	8.44

Oxime, $C_6H_3\begin{cases}OCH_3\\OC_3H_7\\C(NOH)-CH_2-CH_3\end{cases}$.—The above-mentioned ketone was readily converted into an oxime by treating in the usual manner with hydroxylamine. The oxime separates from alcohol in large crystals, melting at 114°. It is easily reverted into the ketone by warming with dilute sulphuric acid, while concentrated sulphuric acid decomposes it with the formation of propionic acid.

Analysis gave the following results:

I. 0.1380 gram gave 0.3323 gram carbon dioxide and 0.1000 gram water.

II. 0.1386 gram gave 0.3334 gram carbon dioxide and 0.1016 gram water.

	Calculated for $C_{13}H_{19}O_3N$.	Found. I.	Found. II.
Carbon	65.82	65.67	65.60
Hydrogen	8.01	8.05	8.14

The formation of ketones from isoapiol- and propylisoeugenol-dibromide may be represented by formulas similar to those given in a previous publication.[1] Two molecules of sodium methylate act upon one molecule of the dibromide with elimination of one molecule of hydrobromic acid and production of an unsaturated ether, $R—C(OCH_3)=CH—CH_3$; this ether yields an unsaturated alcohol by hydrolysis with dilute acids, and this in turn suffers a molecular transformation into the isomeric, saturated ketone.

In connection with the study of the action of sodium alcoholate on the dibromides of compounds containing the propenyl group, we thought it of interest to extend our observations to the behavior of the same reagent towards the dibromides of some unsaturated ketones.

Since propenyl compounds, $R—CH=CH—CH_3$, are so readily converted into ketones, $R—CO—CH_2—CH_3$, it seemed probable that unsaturated ketones,

$$R—CH=CH—CO—C_6H_5,$$

could, by a similar treatment, be changed into diketones of the formula

$$R—CO—CH_2—CO—C_6H_5.$$

The results of our experiments on benzylidene acetophenone have fully substantiated this conclusion. Indeed, the reaction takes place so readily, and the yield of the diketone is so large, that this method seems to be especially well adapted to the preparation of this class of compounds.

Benzylidene Acetophenone, $C_6H_5—CH=CH—CO—C_6H_5$.— The benzylidene acetophenone which served as the starting-point of this work was prepared by the method of Claisen and Claparède.[1] Molecular quantities of benzaldehyde and acetophenone were allowed to stand in an alcoholic solution with a small quantity of ten per cent. sodium hydroxide solution. The resulting con-

[1] This Journal, 19, 827.

densation-product separated from ligroin in large crystals, melting at 57°.

Benzylidene Acetophenone Dibromide,[1] C_6H_5—CHBr—CHBr—CO—C_6H_5.—This addition-product was obtained by adding one molecular proportion of bromine to the cold ethereal solution of benzylidene acetophenone. It crystallized in small, white prisms, and melted sharply at 156°.

Treatment of the Dibromide with Sodium Methylate.—Twenty grams of benzylidene acetophenone dibromide were heated with a solution of sodium methylate, formed by dissolving three grams of sodium in fifty cc. of methyl alcohol, for three hours, on the water-bath. On completion of the reaction, the sodium bromide was dissolved by the addition of water; a dark-colored oil separated, and the mixture was then acidulated with hydrochloric acid, and boiled for two hours. The oil, which had now assumed a dark red color, was separated from the clear liquid, and after standing for a few hours it solidified to a crystalline mass. This was pressed on a porous plate and crystallized from methyl alcohol, yielding red crystals. These crystals melted at 79°–80°, but did not appear quite pure. The red color of the crystals could not be removed by repeated crystallization or by boiling with animal charcoal, but when the compound was distilled at ten mm. pressure the distillate solidified at once to a pure, white, crystalline mass. This was crystallized from methyl alcohol and obtained in large, colorless crystals, melting at 80.5°. It is readily soluble in alcohol and ether, and also in sodium and potassium hydroxides; it is precipitated from alkaline solutions by acids. It is insoluble in sodium carbonate. Ferric chloride imparts a dark-violet color to its alcoholic solution. In all its properties the compound agrees with those of dibenzoyl methane, C_6H_5—CO—CH_2—CO—C_6H_5, which was first obtained by Baeyer and Perkin,[2] and has subsequently been investigated by Claisen.[3]

Analysis gave the following:

I. 0.1257 gram gave 0.3720 gram carbon dioxide and 0.0629 gram water.

[1] Claisen and Claparède: *Ber. d. chem. Ges.*, **14**, 2463; see also Kostanecki and Rossbach: *Ibid.*, **29**, 1492.

[2] Baeyer and Perkin: *Ber. d. chem. Ges.*, **16**, 2134; Perkin: *J. Chem. Soc.*, **47**, 250.

[3] Claisen: *Ber. d. chem. Ges.*, **20**, 655; *Ann. Chem.* (Liebig), **291**, 83.

II. 0.1278 gram gave 0.3773 gram carbon dioxide and 0.0665 gram water.

	Calculated for $(C_6H_5CO)_2CH_2$.	Found. I.	II.
Carbon	80.35	80.49	80.51
Hydrogen	5.35	5.56	5.78

Eight grams of dibenzoyl methane were obtained from twenty grams of benzylidene acetophenone dibromide.

The diketone was further characterized by its conversion into *dibenzoyl-dibromomethane*, $C_{15}H_{10}Br_2O_2$. This separated from methyl alcohol in white crystals, melting at 95°, and agreed in all respects with the compound obtained by Neufville and Pechmann.[1]

The formation of dibenzoyl methane from the dibromide, $C_{15}H_{12}O.Br_2$, is probably accomplished by the production of the unsaturated ether, $C_6H_5—C(OCH_3)=CH—CO—C_6H_5$, which, on hydrolysis with dilute hydrochloric acid, is converted into the unsaturated ketone-alcohol, and then into the diketone.

In order to isolate the unsaturated ether, twenty grams of the dibromide were treated as usual with sodium methylate. On the addition of water to the reaction-mixture, a dark oil heavier than water was thrown out; this was separated and dried over calcium chloride. It showed no trace of bromine, and did not solidify after standing for forty-eight hours, or when placed in a freezing-mixture. When a little of the oil was shaken with dilute hydrochloric acid, it immediately became solid, and after crystallization it gave the melting-point of dibenzoyl methane, 80° to 81°. The oil was distilled under 20 mm. pressure, but it came over without a constant boiling-point and suffered considerable decomposition. The distillate did not solidify on standing or after cooling, and was only partially changed into a solid by agitation with dilute acids. Although this oil could not be obtained in a pure condition for analysis, the readiness with which it is converted into the diketone by the action of dilute acids indicates that it contains the unsaturated ether.

A reaction very similar to the above is found in the action of sodium ethylate upon cinnamic ester dibromide. Leighton[2] found that sodium ethylate acts upon α, β-dibromohydrocinnamic

[1] Neufville and Pechmann: *Ber. d. chem. Ges.*, **23**, 3377.

[2] V. L. Leighton: *Am. Chem. J.*, **20**, 133.

ester to form β-ethoxycinnamic ester, and the latter yields benzoylacetic acid on hydrolysis with hydrochloric acid.

1,3-Diketone, $C_6H_4\begin{cases}OCH_3\\ CO-CH_2-CO-C_6H_5\end{cases}$, *from Anisylidene Acetophenone.*—Anisylidene acetophenone, $C_6H_4\begin{cases}OCH_3\\ CH=CH-CO-C_6H_5\end{cases}$, was prepared by adding twenty cc. of a ten per cent. solution of sodium hydroxide to a solution of twenty-five grams of anisaldehyde and twenty-two grams of acetophenone in 200 cc. of alcohol. After standing for about eight hours, with an occasional shaking, the condensation-product separated in yellow crystals. It was recrystallized from alcohol and obtained in fine, yellow needles, melting at 77° to 78°.

Anisylidene acetophenone dibromide, $C_6H_4\begin{cases}OCH_3\\ CHBr-CHBr-CO-C_6H_5\end{cases}$, was easily produced by adding two atoms of bromine to the cold, ethereal solution of the unsaturated ketone. It crystallized from methyl alcohol in small white prisms, and melted at 140° to 141°.

Thirty grams of the dibromide were heated with a solution of five and one-half grams (two atoms) of sodium in 125 cc. of methyl alcohol for three hours. The reaction product was diluted with water, acidified with hydrochloric acid and boiled for two hours. At the end of this time, the dark oil, which had been thrown out on the addition of water, had completely solidified, and was filtered and dried. The substance had a reddish color, and was purified by distillation under diminished pressure, and crystallization from alcohol. It crystallized in white leaflets, which melted at 131° to 132°. It is only sparingly soluble in methyl and ethyl alcohol and ether, but dissolves readily in chloroform and may be precipitated from its solution in this solvent by methyl alcohol. It is very difficultly soluble in sodium hydroxide. Its alcoholic solution is colored an intense reddish violet by ferric chloride.

Analysis gave the following :

I. 0.1410 gram gave 0.3877 gram carbon dioxide and 0.0718 gram water.

	Calculated for $C_{16}H_{14}O_3$.	Found. I.
Carbon	75.58	74.99
Hydrogen	5.51	5.65

This compound, anisoyl benzoyl methane, was also readily formed when sodium ethylate was used instead of methylate. There appeared to be no difference in the yield, but the product was darker colored when ethylate was employed.

Bromine acts upon this diketone with formation of substitution products. When six and one-half grams (two molecules) of bromine were added to a solution of ten grams (one molecule) of the diketone in 150cc. of ether, a vigorous reaction took place with evolution of considerable hydrogen bromide. On evaporation of the ether, a white, crystalline product resulted; this crystallized from methyl alcohol in well-defined white prisms, and melted at 127° to 128°. This compound is probably anisoyl benzoyl dibromomethane, $C_{16}H_{12}O_3Br_2$, and will be further examined.

When piperonal acetophenone dibromide[1] is treated with sodium methylate according to the above-described process, a compound is obtained which crystallizes in small yellow needles, and melts at 86.5°. This substance is at present under investigation.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 48.]

THE ELECTROLYTIC OXIDATION OF SUCCINIC ACID.

BY CHARLES H. CLARKE AND EDGAR F. SMITH.

Received July 21, 1899.

THE oxidizing action of the current on organic bodies is sure to yield most interesting results. Indeed, the whole organic field remains practically open to investigation along this line. Turn in any direction and ample material will be found for such study. We selected succinic acid as the subject of our investigation. It is, indeed, true that in the past this acid and its salts have engaged the attention of chemists in the electrolytic way, but unfortunately their results are contradictory. No attention was given to the important conditions of current density, voltage, temperature, etc., with the consequence that

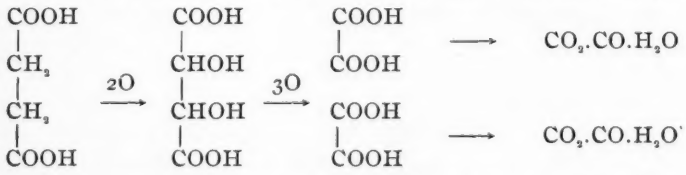
[1] St. v. Kostanecki and Schneider: *Ber. d. chem Ges.*, **29**, 1892.

what has been done electrolytically upon this acid, and, indeed, upon nearly all the acids which have been exposed to the influence of the current, has very little scientific value.

Our aim has been to learn the influence of electrolytic oxygen upon succinic acid. What the products of reduction may be we have not at the present taken pains to ascertain. That is a problem for the future. We have also striven to carefully record the conditions under which we operated and by which our products were produced so that others, if they choose, may repeat and verify them.

The different experiments were conducted in a rather large beaker-glass, using a good porous cup as a diaphragm. The succinic acid was dissolved in definite amounts of sodium hydroxide and known volumes of alcohol. This mixture constituted the anode liquor and it was placed in the porous cup, while the beaker-glass contained sodium hydroxide alone. In those trials in which attention was given to the collection of gases, the mouth of the porous cup was closed with a rubber stopper carrying a small condenser, the latter being suitably connected with a delivery tube leading into an inverted flask or jar, serving as the gasometer.

In considering what the possible result might be in the moderated oxidation of succinic acid, the question naturally arose,—can tartaric acid possibly be produced and then oxalic acid?



Almost every electrolytic study of the acids has made mention of the presence of carbon dioxide, and with us the thought of its possible antecedents was constantly present; hence, we sought to produce and isolate both the tartaric and the oxalic acid.

It may be here remarked that the current used in all the experiments varied from 0.024 to 1.55 ampere for 100 sq. cm. of anode surface. The period of action, as will be seen, ranged from one to ninety-eight hours. When the trial was concluded

the anode liquor had a red color and an aromatic odor. It was acidified with hydrochloric acid, when a great deal of carbon dioxide was evolved. After cooling the liquid was extracted with ether and the watery layer removed by a separatory funnel. Portions both of the ethereal and of the aqueous layers, after the removal of silica and alumina, were carefully freed from other impurities and tested for tartaric acid and oxalic acid. In the first instance recourse was had to the production of the silver mirror, and in the second to the formation of calcium oxalate. The ether extracts of the two experiments showed the mirror, and one of them calcium oxalate. Traces of these acids, therefore, were undoubtedly present. We next endeavored to discover some better means of obtaining and identifying them. During the process of the oxidation, milk of lime was cautiously introduced into the anode chamber. At the expiration of eighteen hours a voluminous precipitate was present. This was filtered out, washed and treated with acetic acid. Much carbon dioxide was evolved, but there remained a precipitate, white in color, which proved to be calcium oxalate. This was then treated with dilute sulphuric acid, filtered and warmed, while potassium permanganate was run into the acid liquid. In this way the presence of 0.0814 gram of oxalic acid was proved.

The coloring-matter of the ethereal extract was isolated. In the purifying process much of it was lost, and the remainder, unfortunately, was also lost through a mishap in making the combustion. The substance, whatever it may prove to be, never appeared in large quantities. It is undoubtedly aromatic in its nature. It melted at 178°, and re-solidified at 169° C.

The gases collected in certain of the oxidations were in the early periods mainly oxygen and carbon monoxide, which later increased in volume and were accompanied by ethylene, methane, and hydrogen.

The appended tables show the working conditions and the corresponding results. To summarize, we may say that the electrolytic oxidation of succinic acid in a divided cell gave *tartaric acid*, *oxalic acid*, some *aromatic bodies*, *oxygen*, *carbon monoxide*, *carbon dioxide*, *ethylene*, *and methane*.

Experiment number.	Succinic acid. Grams.	Sodium hydroxide. Grams.	Alcohol. cc.	Water. cc.	Time. Hours.	N.D.^{100}.	Volts.	Temperature. Degrees.	Remarks.
1	2	4	75	—	6	0.465	3.74	62	Trace of reducing substance in ether extract.
2	2	6	75	—	8	0.361	4.19	65.5	
3	22	46	75	100	5	0.505	2.28	63	
4	17	33	—	100	39	0.461	2.10	22	Obtained tar, although no alcohol was present.
5	12	24	50	10	18	0.409	2.90	22	Ether extract did not react with $C_6H_5NHNH_2$.
6	10	20 cc.[1]	50	10	21	0.359	3.00	22	
7	5	10	50	10	1	0.177	2.74	22	
8	5	50	50	50	18	0.144	2.37	22	
9	5	50	50	50	65	0.024	1.30	22	Muslin cell.
10	5	50	—	50	24	0.035	2.57	23	" "
11	5	50	—	50	24	0.046	2.55	24	" "
12	5	50	—	50	113	0.049	2.55	23	Trace of oxalic acid in water solution.
13	5	50	50	50	12	1.000	3.52	25	
14	5	35	50	65	19	0.262	2.87	24	Trace of oxalic acid in water solution.
15	5	25	50	50	23	0.287	3.22	27	
16	5	50	50	50	20	1.410	4.93	37	Obtained 0.1046 gram $(COOH)_2.2H_2O$.
17	5	50	—	50	47	0.321	2.82	25	Traces of oxalic acid in water solution and ether extract.

[1] Twenty per cent. soda solution used hereafter.

18	5	50	50	100	18	0.420	3.42	29	Obtained 0.0075 gram $(COOH)_2.2H_2O$.
19	5	—	—	—	14	0.685 1.912	1.98	26	Used acetic acid solution of $Pb(C_2H_3O_2)_2$ with lead electrodes. Negative results.
20	5	50	50	50	37	0.757 1.501	3.57	35	Trace of tartaric acid in ether extract. (See Gas Analysis table.)
21	5	50	—	100	19	1.545	3.27	29	See Gas Analysis table.
22	5	50	—	100	21	1.483	3.50	29	See Gas Analysis table.
23	5	50	50	100	55	0.540	3.58	25	
24	5	50	50	100	65	0.212	2.55	23.5	
25	10	100	50	50	38	0.780	2.88	24	
26	10	100	50	50	29	0.286	4.25	23	See Gas Analysis table.
27	10	100	50	50	39	0.773	3.08	24	
28	10	100	50	50	24	0.064	2.57	22	
29	10	—	50	—	98	0.555	2.00	24	Current varied from 0.038–0.899. Nickel electrodes, muslin cell, no tar.
30	10	100	50	50	24	0.756	2.69	28	
31	10	100	50	50	28	0.357	1.83	26	
32	10	100	75	75	55	0.746	2.89	28	See Gas Analysis table.
33	10	100	75	75	68	0.916	2.59	25	See Gas Analysis table.
34	10	100	100	100	82	0.753	2.91	30	See Gas Analysis table.
35	10	100	50	100	70	0.909	2.03	28	
36	10	40	40	—	48	0.737	3.43	29	[1] Two cells { Outer lost 2.72 NaOH = 14.62 per cent. / Middle lost 2.868 NaOH = 11.37 per cent. } Ratio $\frac{1.000}{0.777}$.
37	10	35	35	—	112	0.729	4.30	26	[1] Two cells { Outer lost 6.04 NaOH = 27.55 per cent. / Middle lost 7.24 NaOH = 20.57 per cent. } Ratio $\frac{1.000}{0.746}$.

[1] By this is meant that the cup containing the anode liquor was placed within a larger, similar vessel, and the latter in a large beaker containing the cathode solution.

GAS ANALYSES.

Experiment number.	Sample number.	Oxygen. Per cent.	Ethylene. Per cent.	Carbon monoxide. Per cent.	Methane. Per cent.	Hydrogen. Per cent.
20	1	15.6	9.8	1.3	——	——
21	1	18.0	16.0	4.4	——	——
21	2	79.6	——	——	——	——
22	1	66.7	——	1.0	——	——
25	1	17.2	1.0	10.0	——	——
32	1	3.06	1.96	6.55	44.11	17.90
32	2	3.18	2.72	12.84	24.40	35.88
33	1	77.5	——	3.2	——	——
34	1	18.5	——	1.0	——	——
34	2	2.4	3.1	9.5	31.2	28.9
34	3	41.0	1.0	4.0	——	——
36	1	28.2	3.6	——	——	——
36	2	75.4	5.0	9.6	5.00	0.8
36	3	39.4[1]	14.2	——	——	——
36	4	83.5	7.2	4.3	——	——
37	1	31.0	3.6	3.6	——	——
37	2	60.8	5.8	——	——	——
37	3	66.7	4.6	2.8	——	——
37	4	77.4	2.0	2.6	——	——

NOTES ON THE DETERMINATION OF SULPHUR IN PIG IRON.

BY M. J. MOORE

Received August 4, 1899.

MUCH has been said regarding the inaccuracy of the volumetric method for the determination of sulphur in pig iron, and many good reasons too well-known to mention here, have been given by way of explanation. I will refer, however, to one article by Phillips[2] which illumines some of the dark places admirably.

The writer is not aware that any mention has ever been made that physical treatment was responsible for a great portion of the error, such treatment of course, changing the chemical composition of the iron. It is the practice of nearly all if not all, steel and furnace plants to pour the molten metal into water, this being called a "shot sample." The shot thus formed are taken to the laboratory and crushed in a steel mortar and passed

[1] It was found that the pyrogallic acid was exhausted; hence this discrepancy.

[2] This Journal, 17, 891.

through a sixty or eighty mesh sieve, the powder being subsequently analyzed for silicon and sulphur.

I was brought face to face with the sulphur problem some little time ago and in order that the reader may appreciate my plight some explanation will be necessary.

We were called upon to take samples every hour from the cupolas and mixer, analysis being made for silicon and sulphur on each test continuously for the twelve hours. Our practice at this time was to catch a small test in a sand mold, but it was found necessary to change the mode of sampling because the cupola test was nearly always too hard to drill owing to low silicon and high sulphur which rendered the metal white. The mixer tests, however, could be drilled without any trouble. In order to get around this difficulty we caught shot samples from the cupolas but still continued sampling from the mixer in the old way. Continuing this for twenty-four hours and comparing results it was found that the mixer samples carried more sulphur, apparently, than the cupola samples when the reverse should have been the case especially when low sulphur furnace metal was charged into the mixer. So in order to get comparative results shot samples were caught at the mixer. The next problem that presented itself was to find why there was such an apparent increase of sulphur from the mixer metal to the steel.

To ascertain if there was any difference in sulphur when simply the volumetric method was used, between a drilled sample and a shot sample, samples were caught from the mixer ladle while the metal was being poured into the converter. A portion of the metal was poured into water and the balance into a sand mold. The shot samples were reduced in the usual manner and passed through an eighty mesh sieve and the sand samples were drilled. Determinations for sulphur were made on each, both by the volumetric and gravimetric methods, the latter method according to Blair's "Analysis of Iron and Steel." The results are given herewith :

JOLIET WORKS, ILLINOIS STEEL COMPANY.

Analysis of mixer metal for sulphur, showing that the volumetric method does not give all the sulphur, and that the error is greater in shot samples than in drilled samples.

Shot Samples from Mixer.

Date. 1899.	Blow No.	Volumetric method.	Gravimetric method.	Difference.	Sulphur in residue.	Volumetric sulphur plus residual.	Column 2 minus column 5.	Sulphur in steel.	Remarks.
		1	2	3	4	5	6		
Jan. 9 ..	1026	0.056	0.081	0.025	0.005	0.061	0.020	0.083	Samples were caught from same test ladle.
" 16 ..	2123	0.064	0.096	0.032	0.008	0.072	0.024	0.103	
" 16 ..	2124	0.067	0.095	0.028	0.007	0.074	0.021	0.104	
" 16 ..	2125	0.070	0.103	0.033	0.008	0.078	0.025	0.106	
" 16 ..	2126	0.073	0.103	0.030	0.006	0.079	0.024	0.106	
Mean ..		0.066	0.096	0.030	0.007	0.073	0.023	0.100	

Sand Samples from Mixer.

Date. 1899.	Blow No.	Volumetric method.	Gravimetric method.	Difference.	Sulphur in residue.	Volumetric sulphur plus residual.	Column 2 minus column 5.	Sulphur in steel.	Remarks.
		1	2	3	4	5	6		
Jan. 9 ..	1026	0.068	0.081	0.013	0.0113	0.079	0.002	0.083	Note difference between the volumetric method in column 1.
" 16 ..	2123	0.089	0.098	0.009	0.007	0.096	0.002	0.103	
" 16 ..	2124	0.087	0.101	0.014	0.009	0.096	0.005	0.104	
" 16 ..	2125	0.087	0.103	0.016	0.008	0.095	0.008	0.106	
" 16 ..	2126	0.088	0.103	0.015	0.005	0.093	0.010	0.106	
Mean ..		0.084	0.097	0.013	0.008	0.092	0.005	0.100	

Referring to the mean results we find in column 1 the difference by the volumetric method to be 0.018. This is enough to condemn the practice of taking shot samples.

In column 2 the total sulphur by the gravimetric method is practically the same in each case. In column 3 one exceeds the other by 0.017. In column 4 the residual sulphur in each case is practically the same and in column 6 we see that all the sulphur under shot samples has been accounted for except 0.023 per cent., while under sand samples we are obliged to account for but 0.005 per cent. Or, in one case there is an actual loss of 23.95 per cent., while in the other but a trifle over five per cent.

The results herein given I consider conservative as both

Messrs. Blair and Dudley have pointed out that all the sulphur is not oxidized by the aqua regia method. The writer feels that too much stress cannot be brought to bear on the sulphur question in pig iron as no concordant results can be brought about from the pig iron to the steel.

One of the prominent eastern mills, to account for the error, uses a factor which is far ahead of reporting 100 per cent. of the results wrong as is the case with the evolution method. In conclusion, the writer earnestly invites any criticism if he has made misstatements. His motive has only been to help along the science.

Note.—Since writing the above more experimenting along this line with iron low in sulphur, say No. 1 Bessemer, has brought out the fact that the error between the gravimetric and volumetric methods is not so apparent until about a No. 2 grade is reached.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

A CONTRIBUTION TO THE CHEMISTRY OF BUTTER-FAT.

BY C. A. BROWNE, JR.

Received August 2, 1899.

III. THE CHEMISTRY OF RANCIDITY IN BUTTER-FAT.

THE phenomena attending the development of rancidity in fats have attracted the attention of chemists for many years; even before the beginning of the present century, ere Chevreul had begun his classical "recherches chimiques sur les corps gras," and when the chemical constitution of fats was still unknown, it had been surmised that the physical changes which oils and fats underwent on long keeping were simply the results of oxidation; and this is the view most generally accepted at the present time, notwithstanding the fact that many eminent chemists in the past have sought to explain the development of rancidity in other ways.

From the very complexity of its composition we would suppose butter-fat to be a rather unstable body; if butter-fat is sealed up and preserved in a cold, dark place, it will retain its normal character and appearance for many months, but if kept in a

warm locality with free exposure to the air and light, it will very speedily undergo chemical and physical changes and become, as we say, rancid.

By the term "rancidity" is meant not simply, as is generally supposed, a development of free acid (though this is the general concomitant of rancidity), but any chemical or physical change in the character of a fat from the normal. Fats can be rancid without necessarily being very acid;[1] rancidity, according to the present most commonly accepted understanding of the term, is simply oxidation, and in the early stages of the process butter-fat may loose its characteristic color and smell, and develop an abnormal lardy taste, and still not show an excessive degree of acidity.

That rancidity in butter, as many authorities aver, is primarily the result of the activity of bacteria, is no doubt partly true of whole butter with its lactose, casein, and other constituents to serve as bacterial food, but it is certainly not the case with pure butter-fat which is unable to support micro-organic life. The independent researches of both Duclaux[2] and Ritsert[3] prove beyond question that bacteria cannot thrive in a medium of pure fat, and that all changes which take place in fats on keeping are wholly the results of an oxidation, conditioned to a great extent by exposure to light. The distinction between rancid butter and rancid butter-fat should be borne in mind, since the former condition may prevail without the latter. We have paid but little attention to the development of rancidity in whole butter,[4] and will make this a subject for future study. The present work is confined entirely to those changes which the pure fat undergoes after its separation from all impurities.

[1] We believe v. Klecki was the first to distinguish between the terms rancidity and acidity. *Ztschr. anal. Chem.*, **34**, 633 (1895).

[2] Annal. de l'Institut Pasteur, 1888.

[3] Untersuchungen über das Ranzigwerden der Fette.

[4] Lactic acid is always found in both fresh and rancid butter, but never in rancid butter-fat. We have found 0.08 per cent. of lactic acid in fresh butter made from ripened cream, and 0.12 per cent. in a rancid butter. The latter sample also contained 0.23 per cent. of free volatile acids, having a mean molecular weight of 94, to which acids the rancid odor and taste of the butter were no doubt largely due.

The statement frequently met with that rancidity in butter is produced by the action of a butyric ferment upon the fat with the formation of butyric acid, is not warranted. It is a well-known fact that milk sugar may pass by fermentation through lactic into butyric acid, and there is every probability that, under favorable conditions, much of the lactose in butter is converted in this way into volatile acid products.

The part which bacteria play in the spoiling of butter has been studied but little up to the present time; the question is one well worth the attention of bacteriologists.

The three factors most active in the production of rancidity in fats are openness to air, exposure to light, and degree of warmth. Given sufficient time, decomposition may occur with the suppression of any one or even two of these elements, but it is of course most rapid when all three conditions are favorable.

In the development of rancidity in butter-fat, under the usual conditions named above, there are observed first of all several changes as regards color, odor, taste, and general appearance. The sample examined begins first to acquire a lighter color; this change appears first on the surface, and the parts most exposed to the light, from which points the action spreads slowly downward until finally the whole mass has become bleached.[1]

With this loss of color we notice also the development of a lardy odor and taste; as the period of rancidity advances the odor increases in pungency, while the taste, which at first was not markedly acid, becomes exceedingly burning and unpleasant. In addition to the above we observe some changes in consistency; the sample, which originally was firm and solid in texture, begins to take on a granular look and finally turns, after many months, into a semisolid pasty mass.

If we determine the various constants of a butter-fat at different periods of rancidity, we notice still other important changes, as can be seen from the following table:

TABLE XII.

Age of sample.	Degrees rancidity.	Acid number.	Saponification number.	Ether number.	Reichert number.	Iodine number.	Oleic acid. Per cent.
Fresh	0.9	0.48	228.1	227.6	15.63	34.95	38.79
1 week	2.3	1.28	230.3	229.0	15.80	34.55	38.35
1 month	19.4	10.90	241.0	230.1	17.00	28.40	31.52
2 months	51.5	28.84	260.0	231.2	18.75	14.35	15.93
4 months	53.5	30.00	262.1	232.1	19.80	11.15	12.38
8 months	63.2	35.38	269.3	233.9	21.13	8.55	9.49

We observe with the development of rancidity, a decided increase in the acid, saponification, and Reichert numbers, a slight increase in the ether number, and a very marked decrease in the iodine absorption.

"Degrees rancidity" is a constant employed by many chem-

[1] This observation pertains only to samples of natural color; with butters artificially colored the bleaching is not always evident, showing that certain butter colors are not affected by the development of rancidity.

ists as another way of expressing the free acid in fats, and is placed in this and succeeding tables only for the purpose of comparison. It was introduced into fat analysis by Stockmeier[1] and represents the number of cubic centimeters of normal alkali required to neutralize the free acid in 100 grams of fat: the number of cubic centimeters of tenth normal alkali necessary to neutralize the free acid in ten grams of fat would also give "degrees rancidity;" one degree rancidity would correspond to an acid number of 0.56.

The effects of rancidity upon the composition of butter-fat are also shown by Table XIII, where the chemical constants of four different samples are given in both the fresh and rancid conditions.

TABLE XIII.

Butter-fat.	Condition.	Degrees rancidity.	Acid number.	Saponification number.	Ether number.	Iodine number.	Oleic acid. Per cent.	Acetyl number.	Insoluble acids. Per cent.	Glycerol. Per cent.
1*a*	Fresh	0.80	0.45	229.9	229.5	33.93	37.66	4.8	87.20	12.54
1*b*	Rancid	2.18	1.22	232.3	231.1	29.96	33.26	7.6	86.80	12.40
2*a*	Fresh	0.89	0.50	223.9	223.4	34.49	38.28	3.5	88.96	12.21
2*b*	Rancid, 1 month	12.66	7.09	233.7	226.6	28.69	31.85	10.9	85.06	12.02
3*a*	Fresh	0.98	0.55	232.6	232.1	29.56	32.81	4.1	86.41	12.69
3*b*	Rancid, 2 months	20.95	11.73	247.7	236.0	19.76	21.93	15.1	80.42	12.35
4*a*	Fresh	0.93	0.51	225.6	225.1	34.92	38.76	3.8	88.46	12.33
4*b*	Rancid, 3 months	26.43	14.80	245.3	230.5	22.55	25.03	18.0	81.15	11.67

Sample 1 was exposed for three months to air and light in a cold room during winter; *a* represents the unoxidized bottom layer, and was unchanged; *b* represents the upper oxidized part which was bleached and had an abnormal taste and smell. Samples 2*b*, 3*b* and 4*b* were allowed to become rancid in a warm place, with free exposure to air and light.

In addition to the facts previously observed we note from the above table that with the advancement of rancidity there is an increase in the acetyl number and a decrease in the percentages of insoluble acids and glycerol. Other changes produced in the

[1] *Vierteljahrsschrift Nahr. und Genussmittel* (1889), 428. According to Stockmeier, a butter-fat showing more than eight degrees rancidity should be condemned as unfit for use. Chemists have recognized the impossibility of fixing any such arbitrary standard as this: a butter-fat may show only two or three degrees rancidity and still be offensive to our organs of sense, which latter, we may say, are far superior to any chemical methods in forming judgments as to the palatability of foods.

chemical and physical constants of butter-fat by rancidity will be presented in the course of the article.

EFFECTS OF RANCIDITY UPON THE ACIDS OF BUTTER-FAT.

It is a well-known fact, and one wholly confirmed by the preceding tables, that the oleic acid is the constituent of butter-fat most susceptible to chemical change; being an unsaturated compound it absorbs oxygen with great avidity at the points of unsaturation, yielding either oxy-compounds or decomposing into simpler bodies of lower molecular weight. It is impossible to express by chemical equations either of these changes, owing to the complexity of the reaction and the great variety of products formed.

By means of oxidizing agents oleic acid has been found to yield not only all the members of the homologous series from formic to capric acid, but also certain dibasic and oxy-acids.[1] While the oxidation process itself, which takes place with oleic acid in the development of rancidity, is less violent than that produced by artificial means, we may say that the character of the decomposition products is to a considerable extent the same.

A. Scala[2] detected in a strongly rancid olive-oil formic, acetic, butyric, and oenanthylic acids, also several dibasic acids of the type $C_nH_{2n-2}O_4$, among others azelaic and sebacic acids; besides these another acid was isolated which, from the analysis of its barium salt, was identified as dioxystearic acid. The same authority also shows that the saturated acids could take no part in the formation of these decomposition products, since they offer a complete resistance to oxidation; small portions of stearic and palmitic acid, on long standing, were found to suffer under ordinary conditions no change in weight; oleic acid, on the other hand, after ten months' exposure to the air and light, increased in weight over eight per cent. As an additional confirmation of this, it was found that the increase in weight, which different fats underwent on becoming rancid, was in direct proportion to their content in oleic acid.

The amount of oxygen which butter-fats absorb on becoming rancid we have found to vary somewhat with the conditions. A

[1] Watts' Dictionary of Chemistry, Edition of 1892, 3, 637.

[2] Staz. sperim. agr. ital., p. 613 (1897). Abstract in Biedermann's *Centrbl. für Agriculturchemie*, March, 1899, p. 196.

thin layer of butter-fat, exposed in a melted state to the action of air and light, gained at the end of two weeks 1.54 per cent. of the original weight; it then began to lose, and at the end of two months had lost 1.94 per cent. of the weight of the sample when fresh. Chemical change proceeds much faster with fats if melted, so that the preceding example can not be taken as a fair illustration of what takes place under ordinary conditions.

The following elementary analysis of two butter-fats, one fresh and the other rancid, gives some information as regards the amount of oxygen absorbed during rancidity.

TABLE XIV.

Butter-fat.	Condition.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
1	Fresh	75.17	11.72	13.11
2[1].....	Rancid, 2 years old	73.88	11.57	14.55

These results show that the effect of rancidity is to cause a decrease in the percentages of carbon and hydrogen, with a corresponding increase in the percentage of oxygen. Similar results were secured by Lenz[2] in the case of fresh and rancid horse-fat.

Inasmuch as the iodine number is dependent upon the amount of oleic acid, it is obvious enough that this constant should show a decrease as the period of rancidity advances. We have given in Tables XII and XIII the percentages of oleic acid corresponding to the various iodine numbers. There is some uncertainty among chemists as to the accuracy of calculating the per cent. of oleic acid from the iodine absorption;[3] this uncertainty would be still greater in the case of rancid fats, where there is the possibility that other unsaturated compounds besides oleic acid may for the time exist.[4]

The increase in the saponification number as the period of rancidity advances, can be explained only by the breaking up of higher acids into acids of lower molecular weight,—an explanation which is confirmed by the decrease observed in the per-

[1] This sample, which was badly decomposed, stood during the time indicated in a cool place near a window, where the light could have its full effect.

[2] *Ztschr. anal. Chem.*, p. 441 (1889).

[3] For a discussion of this point consult Wiley's Agricultural Analysis, **3**, 367. See also this Journal, **21**, p. 811.

[4] Such an error would not alter the main facts of the case, however, as the effect would be to magnify rather than diminish the actual percentage of oleic acid.

centage of insoluble acids, and by the increase which takes place in the Reichert number.

It was thought that a determination of the mean molecular weight of the volatile acids from rancid butter-fats would throw some light upon the character of the lower acids formed by decomposition, but the results were in some ways disappointing. The majority of the experiments showed but little difference between the molecular weights of the volatile acids from the fresh and rancid samples, the general tendency seeming to be towards a slight decrease in this constant, as the butter-fat became rancid. The mean molecular weight of the volatile acids formed by decomposition would appear from this to have nearly the same value as that of the volatile acids in the fresh sample; this would bear out the view that, in the breaking up of the oleic acid, several different soluble acids are formed, the lower members of the series apparently being produced in the largest quantity.

The free acid, which soon makes its appearance in all rancid fats, is due not simply to oleic acid and its decomposition products, but to other acids as well. In the development of rancidity there seems to be a gradual breaking up of all the glycerids. Samples of tripalmitin which we have prepared from butter-fat, while much more stable than the parent substance, show after long standing the same tendency to become rancid and develop free acid. This is true of other glycerids as well, the acid part of the molecule splitting off from the glycerol base with the probable disruption of the latter. In the case of complex oleins (oleobutyrin, oleopalmitin, etc.), the changes which so soon effect the oleic acid would no doubt hasten the disintegration of the entire glycerid. The first change which manifests itself in fats on becoming rancid is apparently an oxidation of some oleic acid within the molecule, as changes appear in physical and chemical properties before any considerable development of free acid. Butter-fat No. 1 in Table XIII affords us a good illustration of this; the upper oxidized layer of this sample, when compared with the lower unchanged part, shows a decrease of over four per cent. in oleic acid, and an increase of nearly three units in the acetyl number, while the acid number of the

rancid portion appears but eight-tenths higher than that of the unchanged fat.

A determination of the iodine absorption of the free insoluble acids throws some light upon the proportion of free oleic to other acids. 100 grams of a rancid butter-fat were shaken with an equal quantity of hot ninety-five per cent. alcohol. After cooling completely in ice-water, the alcoholic solution was poured through a filter and exactly neutralized with a dilute solution of potassium hydroxide, using phenolphthalein. The solution was then heated on the steam-bath until all alcohol was evaporated, when the residue was treated with 100 cc. of hot water. The soapy solution, after standing on the bath for a little while to allow any fat which may have been removed by the alcohol to rise, was filtered, cooled and thoroughly extracted with ether to remove all traces of unsaponified matter. An excess of dilute hydrochloric acid was then added to decompose the soaps, and the insoluble acids collected in the usual way.

The iodine number of the free insoluble acids obtained from a rancid butter by this process was 18.47, corresponding to 20.50 per cent. of oleic acid. Thum[1] found in experiments with palm- and olive-oil that the free fatty acids in rancid oils contained oleic acid in almost exactly the same proportions as in the neutral fat. Similar results were obtained by Spaeth[2] in the case of rancid lards. Such experiments show that the method, so commonly practiced, of calculating the total acidity of rancid fats to oleic acid alone is by no means accurate.

The amount of free volatile or soluble acids in rancid butter-fats is much smaller than might be expected. A comparison of the acid numbers, and the acid numbers for the water-soluble acids alone, indicates that in the early stages of rancidity at least, the free soluble acids bear to the total free acids a relation smaller than that existing between the soluble acids and total acids of normal butter-fat. The following table will make this clearer:

1 *Ztschr. angew. Chem.*, 482 (1890).
2 *Ztschr. anal. Chem.*, 471 (1896).

TABLE XV.

Butter-fat.	Character of sample.	Total acid number (t).	Water soluble acid number (s).	Relation $\left(\frac{s}{t}\right)$
1.....	Rancid, 1 month	7.09	0.84	0.1184
2.....	" 2 months	11.73	1.57	0.1338
3.....	" 8 "	35.38	5.99	0.1664
	Total acids of butter-fat,	228.5[1]	40.5[2]	0.1772

The determination of the value t, or ordinary acid number, has already been described[3] and need not be mentioned here. The value s, or water-soluble acid number, represents the milligrams of potassium hydroxide necessary to neutralize the free water-soluble acids in one gram of fat, and is found by washing about ten grams of the rancid fat with successive portions of boiling distilled water until all acid is removed, and then titrating the filtrate with tenth-normal alkali.

It is seen from the preceding table that the value $\frac{s}{t}$ increases with the period of rancidity, and approaches the relation existing between the total and soluble acids of normal butter-fat; this relation would no doubt be equaled or even exceeded by fats in a very advanced stage of rancidity. The results in Table XV confirm the statement of Bondzynski[4] and Rufi that rancidity in butter-fat is due principally to the formation of free insoluble acids, and that free volatile or soluble acids are not found to any extent except in a very advanced stage of decomposition.[5] This would not only indicate that the glycerides of the soluble acids in butter-fat are the most stable, but also leads to the following very pertinent question. If the statement previously made in regard to the breaking up of oleic acid into lower soluble acids be correct, *why is it that these acids do not appear to any great extent in the free condition?* That such acids are apparently formed was shown in Table XII by the increase in the Reichert number which fats undergo on becoming rancid, and that they are formed to a considerable extent, seems evident from the decrease which takes place in the percentage of insoluble acids, as is seen from Table XIII.

[1] The average saponification number of butter-fat. This Journal, **21**, 613. Table I.

[2] The milligrams potassium hydroxide required to saponify the soluble acids in one gram average butter-fat. *Ibid.*, p. 628.

[3] This Journal, **21**, 614.

[4] *Ztschr. anal. Chem.*, 1 (1890).

[5] Spaeth found the same true of rancid lard. *Ibid.*, 479 (1896).

There are several possible ways of explaining this non-appearance of the soluble acids formed by decomposition. There is the possibility that the oleic acid, when in the glyceride form, may split up into a soluble and an insoluble acid, the soluble acid remaining in combination with the glycerol base; this hypothesis, however, does not seem a tenable one since a large amount of free oleic acid is found in rancid fats, as was shown by a preceding experiment.[1] There is also the possibility that esters of the soluble acids may in some way be formed, but this view seems no more plausible than the other; such esters have been found in whole butter,[2] but we have not been able to detect their presence in rancid fats.

The best explanation of this difficulty which we have been able to arrive at is the following: the first products formed by the decomposition of oleic acid are not of an *acid* but of an *aldehyde* nature; these aldehyde bodies are further changed by oxidation into soluble acids, but this takes place only in a very advanced stage of rancidity, which would explain the fact, already referred to, that free soluble acids are not formed to any great extent except in rancid fats of considerable age. By the action of alcoholic potash, aldehydes are decomposed into acids, and small quantities of dark resinous compounds;[3] this would account for the fact that the soluble acids of decomposition do not appear until after saponification, and would also explain the brown coloration which all rancid fats undergo when treated with alkalies.

The presence of aldehydes in rancid fats is indicated on other than theoretical grounds. The cocoanut-like odor, so peculiar to butter-fat in the early stages of rancidity, and the very pungent smell developed later, are probably due to aldehyde products. Spaeth[4] has called attention to the reducing action which all rancid fats have on Becchi's silver solution as an evidence of these bodies, while E. von Raumer[5] has detected their presence by the aid of Schiff's reagent. The latter test we have found to be one of extreme delicacy.

[1] This article, p. 982. Indications are that most of the changes which affect the oleic acid take place after the latter has been set free.

[2] Amthor: *Ztschr. anal. Chem.*, 10 (1899).

[3] Watts' Dictionary of Chemistry, second edition, 1, 111.

[4] *Ztschr. anal. Chem.*, 487 (1896).

[5] *Ibid.*, p. 487.

Schiff's reagent is prepared by saturating a solution of rosaniline acetate with sulphur dioxide gas, and allowing it to stand in a stoppered bottle until completely decolorized. In making the test about one cc. of the melted fat is placed in a test-tube with ten cc. of hot water and thoroughly shaken; one cc. of the reagent is then added and the contents of the tube shaken up a second time. If aldehydes are present the fat and liquid underneath will be colored a splendid violet,—the intensity of the coloration being proportional to the rancidity of the sample. Fresh butter-fat gives no test with Schiff's reagent, even after many hours' standing; with fats of moderate rancidity the coloration varies from a pink to a bright cherry-red, while with very old and rancid specimens the layer of melted fat is colored a very dark purple, the liquid underneath being a deep violet. The fact that both fat and liquid were colored would show that aldehydes were present in both soluble and insoluble forms. After saponifying a rancid fat and decomposing the soap solution with an excess of hydrochloric acid, the Schiff test was applied with negative results,[1] thus proving beyond all doubt that the action of alkalies is to completely destroy all compounds of an aldehyde nature.

The existence of aldehydes in rancid fats, and their behavior with saponifying agents, explains another point which we have not yet referred to in connection with Tables XII and XIII. It will be seen from these tables that with the development of rancidity there is a noticeable, but not excessive, increase in the ether number. The true ether number of a rancid fat, representing as it does the milligrams of potassium hydroxide necessary to saponify the neutral fat in one gram of substance, would naturally be lower than that of a fresh sample, since with the breaking up of the glycerides the quantity of neutral fat becomes steadily less.[2] The presence of aldehydes, however, causes a vitiation in the true ether number; these bodies are not affected in the determination of the acid number, but when the alcoholic potash is added in excess for the determination of the saponification number, the aldehydes, as has been shown, are decom-

[1] The insoluble acids were slightly tinged, but strange to say the coloration was not as pronounced as with the acids from fresh butter-fat. We attribute this reaction in the insoluble acids to a slight decomposition of the oleic acid subsequent to the saponification.

[2] This supposition is confirmed by the decrease which takes place in the percentage of glycerol.

posed into acids, to neutralize which an excess of potassium hydroxide is required greater than that necessary to saponify the neutral fat alone. This vitiation of the ether number is much greater than the tables indicate, owing to the fact just mentioned that the true ether number of a fat steadily decreases with the advancement of rancidity.

We have already alluded to the fact that oxy-acids are found in all butter-fats irrespective of age, and the statement was made in a previous article that the low acetyl number, which fresh butter-fat shows, and the steady increase of this constant with age, suggest that these compounds are entirely after-products, and do not exist in the milk-fat before secretion. Experiments already mentioned[1] indicate that the oxy-acids are derived entirely from oleic acid, dioxystearic acid being principally formed.

The following table, compiled from results given in Tables XII and XIII, offers a few interesting comparisons, and gives some idea of the probable manner in which the oleic acid of butter-fat is decomposed.

TABLE XVI.

Butter-fat.	Condition.	Oleic acid. Per cent.	Insoluble acids. Per cent.	Loss in oleic acid. Per cent.	Loss in insoluble acids. Per cent.	Acetyl number.	Increase in acetyl number.	Increase in oxy-acids. Per cent.[2]
No. 1..	Fresh	38.28	88.96			3.5		
No. 1..	Rancid	31.85	85.06	6.43	3.90	10.9	7.4	1.78
No. 2..	Fresh	32.81	86.41			4.1		
No. 2..	Rancid	21.93	80.42	10.88	5.99	15.1	11.0	2.51
No. 3..	Fresh	38.76	88.46			3.8		
No. 3..	Rancid	25.03	81.15	13.73	7.31	18.0	14.2	3.28
No. 4..	Fresh	38.79	87.72					
No. 4..	Rancid	9.49	72.03	29.30	15.69			

We observe from the above table that the loss in insoluble acids accounts for but little more than half the loss in oleic acid; the ratio seems to be a fairly constant one, and averages about fifty-five per cent. This figure, then, may be taken to represent approximately the amount of oleic acid in the loss which is con-

[1] By Scala, this article, p. 979.

[2] Calculated as dioxystearic acid by the formula, $x = \frac{100\,cm.}{a(56100 - 42c)}$. This Journal, 21, 817.

verted into lower soluble acids.[1] Calculating the increase in the acetyl numbers to dioxystearic acid will make up about twenty-five per cent. more of this loss in oleic acid, thus leaving about twenty per cent. still unaccounted for; the formation of insoluble aldehyde products[2] during the saponification may explain this discrepancy.

Owing to the formation of oxy-acids the chemical and physical characteristics of the insoluble acids from butter-fat suffer marked changes with the development of rancidity. The following constants were determined on the insoluble acids of butter-fat No. 4 in the preceding table.

TABLE XVII.

Condition of butter-fat.	Mean molecular weight of insoluble acids.	Melting-point of insoluble acids.
Fresh	260.2	40.2° C.
Rancid	273.7	44.7° C.

These differences are such as one would expect; the increase in the mean molecular weight and melting-point of the insoluble acids, both being the results of the formation of oxy-acids.

EFFECTS OF RANCIDITY UPON THE GLYCEROL OF BUTTER-FAT.

One of the most disputed points in connection with the rancidity of fats is that concerning glycerol. A large number of chemists hold that, as fats become rancid, glycerol is liberated in the free state, and cite the instance of palm-oil, which seems to split up almost quantitatively into its fatty acids and glycerol; in contradistinction to this many chemists, having tested rancid fats for free glycerol with totally negative results, claim that no free glycerol is formed; other chemists, attempting to reconcile these conflicting views, take the somewhat intermediary position, that fats on becoming rancid are decomposed into free acid, and free glycerol, but that the latter is almost immediately destroyed by oxidation.

A quantitative decomposition of a perfectly pure and dry neutral fat into its glycerol and acids, is manifestly impossible, as

[1] Including those already existing and those formed by the action of alkali on the aldehydes.

[2] The presence of aldehyde condensation products, resin, etc., which are always formed by alcoholic potash, would produce an error in the determination of the insoluble acids. The insoluble acids from rancid butter-fats are invariably colored by these bodies, the coloration varying from a yellow to a dark brown according to the rancidity of the sample.

such a reaction would require the presence of a large amount of water.

$$C_3H_5(RO_2)_3 + 3H_2O = C_3H_8O_3 + 3RO_2H.$$
$$\text{Fat} + \text{water} = \text{glycerol} + \text{fatty-acid.}$$

To reason from the analogy of palm-oil is not permissible; this oil is abnormal in many ways, containing, as it does, some twelve per cent. of free acid, even when fresh, with a considerable amount of moisture and other impurities.[1]

The percentage of glycerol in rancid fats cannot be calculated from the ether number, owing to the vitiation in this constant previously referred to. The process of separating the glycerol from other bodies, and determining its percentage by direct weighing, is never accurate and would be still less applicable with rancid fats, where the glycerol would be contaminated with various impurities. A statement made by some chemists that fats undergo an increase in the percentage of glycerol on becoming rancid, is undoubtedly due to some such faulty method of analysis as the above.

The determinations of glycerol in rancid fat made by us were all performed according to the method of Benedikt and Zsigmondy, as previously described.[1] The results, which are tabulated in Table XIII, all show a decrease in the percentage of glycerol as the butter-fat became rancid, the decrease being proportional to the rancidity of the sample.

It is impossible to say just how this loss of glycerol is incurred; it no doubt takes place in the separation of the various fatty acids, and there is good reason to suppose that these acids, since they do not occur as anhydrides, have seized upon the glycerol radical for the elements of water necessary to their formation. If this theory be correct, very little if any glycerol would appear in the free condition; we have examined rancid butter-fats for free glycerol by washing with large quantities of boiling water, and testing the filtrate by the Benedikt and Zsigmondy method. Small quantities of oxalic acid were formed, equivalent to from one-tenth to two-tenths per cent. glycerol; this may have been derived, however, from the oxidation of water-soluble aldehydes, as well as from glycerol. We believe a small amount of acrolein

[1] According to Benedikt the percentage of impurities with different grades of palm-oil ranges from 0.50 to 17.00 per cent. Analyse der Fette, third edition, p. 525.

[2] This Journal, 21, 621.

is formed from glycerol in the development of rancidity and attribute the pungent irritable odor which all rancid fats give off—especially on being warmed—to the presence of this compound.

EFFECTS OF RANCIDITY UPON THE PHYSICAL CONSTANTS OF BUTTER-FAT.

The alterations in chemical composition, which butter-fats undergo with age, produce very decided changes upon the physical constants.

It is a well-recognized fact that as rancidity is developed the specific gravity of fats increase. The specific gravity $\frac{40°}{15.5°}$ C. of fresh butter-fat was found to range from 0.9050 to 0.9102; the values of this constant for rancid butter-fats, at the same temperatures of comparison, were considerably higher, and varied between 0.9195 and 0.9252. This increase is easily explained by the fact that in the development of rancidity the oleic acid, of low specific gravity, is changed by oxidation into compounds of greater density. This is in full agreement with the statement of Brühl[1] that "by the addition of oxygen the specific gravity of bodies always exhibits a marked increase, no matter what the product of oxidation may be, whether acid, alcohol, oxy-acid, or other in character." It is owing to this increase in specific gravity that the viscosity of fats becomes greater, as the period of rancidity advances.

In regard to melting-point rancid butter-fats exhibit the greatest irregularity, and we have finally come to the conclusion that it is impossible to make a satisfactory determination of the melting-point of butter-fats in a very advanced stage of decomposition. In the early period of rancidity the melting-point is somewhat higher than that of the fresh butter-fat; the increase, which is probably due to the formation of oxy-compounds of higher melting-point, is not a marked one, however, the differences ranging from 0.1° to 1.5° C. A quite characteristic phenomenon, observed with some rancid butter-fats, was that of double melting-point. As an example a rancid butter-fat, by the capillary tube method,[2] melted at 24.2° C.; after keeping the

[1] *Ann. Chem.* (Liebig), 211, 128. See note 2, p. 992 of this article.

[2] The official method could not be used with any degree of success, owing to the solubility of decomposition products in alcohol.

temperature at this point for a few minutes the fat solidified again and, on increasing the heat, remelted at 33.4° C.[1] Samples of excessive rancidity do not exhibit this trait; such fats will usually begin to liquefy at from 22° to 24° C., but will remain turbid from insoluble particles, and will not become perfectly clear until the temperature reaches 35° to 40° C. This behavior is probably due to the presence of two classes of decomposition products; those of low melting-point, such as fatty aldehydes and lower acids, and those of high melting-point, such as oxy-acids. In this way too would be explained the peculiar semi-fluid consistency, which very rancid fats acquire, fresh butter-fat, under the same conditions, remaining firm and solid.

The development of free acid, which takes place in ranoid fats, has a very marked effect upon the critical temperature of dissolution. This simple test devised by Crismer[2] is especially valuable in testing fats and merits a brief description in this connection. About one-half cc. of melted butter-fat is placed in a slender test-tube with twice its volume of absolute alcohol. The tube is closed with a cork, through which a thermometer is passed so that its bulb is entirely covered with the solution and does not touch the walls of the tube. The tube and thermometer thus prepared are passed through a tightly fitting cork into a larger tube partly filled with water; the whole is then gently heated, with constant shaking, until the mixture of alcohol and butter-fat becomes perfectly clear. The temperature at which turbidity appears, after allowing the apparatus to cool, is noted as the critical temperature.

Crismer has observed that with rancid butter-fats the critical temperature is materially lowered, and that this lowering is proportional to the acidity of the fat. By neutralizing such products with weak alkali and washing the fat with hot water, the normal critical temperature was found to be restored; we have secured the same result by washing the rancid fat with alcohol.

The mean critical temperature of several fresh butter-fats, examined by us according to the above method, was 57° C.;[3]

[1] Other instances are known of fatty bodies showing double melting-point. Palmitin melts at 50.5° C. and again at 66.5° C. Analyse der Fette, third edition, p. 44.

[2] *Bull. Assoc. belge*, 10, 312 (1896). Abstract in *Analyst*, 22, 252, 71.

[3] Of the various rapid tests for adulterated butters this is one of the most reliable. Crismer found for pure butter-fat critical temperatures ranging from 50° to 57° C., and for margarine and mixtures results between 64° and 78° C.

rancid butter-fats gave results ranging from 45° to 50° C. according to the degree of acidity.

It is very interesting to note the effect which rancidity has upon the refractive power of fats. All observers[1] agree in this that the refractive index of a fat increases with the development of rancidity, but differ as to the explanation of the phenomenon.

Unfortunately we had no refractometer in the early stages of our work, and so no comparative readings could be made on the various rancid butter-fats used in these experiments. Recently, however, we have been able to make a large number of refractometer readings on various fresh and rancid butter-fats, and in all cases found that the rancid samples gave a higher refractive index. The readings were made on a Pulfrich instrument, the yellow sodium ray (D) being used.

TABLE XVIII.

	Range in refractive indices, 30°C.		Mean.
Fresh butter-fats.....	1.45872	1.45922	1.45897
Rancid " "	1.45982	1.45992	1.45987

Instead of using the refractive index as a means of comparison, we have preferred to use the specific refractive power. The coefficient of refraction varies greatly with the specific gravity, so that a determination simply of the refractive index leaves one very much in doubt as to whether or not any changes observed may not be due wholly to differences in density.

The specific refractive power is calculated from the formula[2] $\frac{N-1}{D}$, in which N equals the refractive index of the substance and D its specific gravity.

TABLE XIX.

	Specific gravity $\frac{30°\,C}{15.5°}\left(D\right)$.	Refractive index 30° C (N).	Specific refractive power $\left(\frac{N-1}{D}\right)$.
Fresh butter-fat.....	0.91260	1.45897	0.50292
Rancid " "	0.92571	1.45987	0.49677

It is seen that the specific gravity and refractive index of rancid butter-fats is higher, but that the specific refractive power is lower. These results are in perfect accordance with the

[1] See articles by Spaeth and Scala already referred to.

[2] Landolt : *Ber. d. chem. Ges.*, 15, 1031.

observations of Brühl,[1] that by the addition of oxygen the specific gravity of bodies shows a marked increase and that the same change takes place but to a less degree with the refractive index, but that the specific refractive power is always *smaller* in the body richer in oxygen.[2]

In view of this, since the percentage of oxygen increases in fats as they become rancid, the changes which affect the refractive power find an adequate explanation.

Another important effect of rancidity upon fats is the marked decrease in the calories of combustion. This is a fact which requires but little explanation. Rancidity is in reality only a slow process of combustion, like other forms of oxidation; it is therefore plain that a certain amount of heat is given off by fats in the development of rancidity and that in consequence thereof the original heat-producing power must suffer a decrease.[3] The following experiments performed on a fresh and rancid butter-fat will illustrate this. A Hempel-Atwater bomb calorimeter[4] was used in the work.

TABLE XX.

	Chemical composition.			
	C. Per cent.	H. Per cent.	O. Per cent.	Calories.
Fresh butter-fat.....	75.17	11.72	13.11	9366.
Rancid " "	73.88	11.57	14.55	9095.

CONCLUSION.

We have attempted to give in the preceding pages a few of the main facts in connection with the subject of rancidity. The point was made in the beginning of this paper that the nature of the chemical and physical changes, which take place in the decomposition of fats, is one largely dependent upon conditions.

[1] Die chemische Constitution organischer Körper in Beziehung zu deren physikalischen Eigenschaften. By J. W. Brühl. *Ann. Chem.* (Liebig), 211, 121.

[2] More fully expressed in the language of the original. *Ibid.*, p. 128. "Aus dieser Tabelle ergiebt sich, dass durch die Addition von Sauerstoff die Dichte der Körper stets sehr bedeutend zunimmt, gleichgiltig, welche Art von Verbindung, ob Säure, Alkohol, Oxysäure, u. s. w., hierdurch gebildet wird. Gleichzeitig, aber weit schwächer, wächst auch der Brechungsindex. Dagegen ist die auf gleiche Dichte reducirte brechende Kraft, oder das Brechungsvermögen, bei dem an Sauerstoff reicheren Körper stets kleiner."

[3] Brühl: Op. cit. supra, p. 126. "Die Verbrennungswärme der Körper sinkt sowohl durch Vereinigung derselben mit Sauerstoff, * * * * * *, oder durch Ersetzung von Wasserstoff durch Sauerstoff."

[4] Seventh report of the Storrs Agricultural Experiment Station, Conn., p. 135.

The results of the present article were obtained under only one particular set of conditions; *viz.*, those most favorable to the production of chemical change. Had the conditions of warmth, light, and exposure to the air been varied, a difference no doubt would have been observed in the degree and character of some of the changes produced. Further investigations as to these points are greatly to be desired.

As we found it difficult to make the distinction between normal and abnormal butter-fats a sharp one, so are we perplexed if we try to draw the line between the qualities fresh and rancid. Butter-fat, as fresh as it can possibly be obtained, gives distinct acid and acetyl numbers, and these changes were no doubt initiated before the cream was separated and churned; we may say therefore that, in a certain chemical sense, fresh butter-fat itself is rancid. If chemical changes begin thus early, we naturally ask ourselves, to what limits can this process of decomposition in fats go? This is a difficult question to answer for we know of no instances where fats were kept a sufficient length of time to enable any conclusions as to this point being formed. The ultimate products of oxidation would of course be water and carbon dioxide, but under ordinary conditions this result would hardly be reached; we are probably safe in saying that chemical change will not cease until all the glycerides are decomposed and the oleic acid is completely changed; whether or not other changes of a different order, such as the formation of paraffin bodies, may set in, is wholly a matter of conjecture.

Owing to lack of time we were unable to make a closer study of the various decomposition products formed in butter-fat by rancidity; nothing whatever was done toward the separation and identification of the various aldehydes, acids and other bodies produced in rancid fats, and this we feel to be a serious omission to completeness. As we stated at the beginning, these studies upon butter-fat were conducted in a very desultory manner, being pursued only as other laboratory duties permitted; this we offer as an excuse for the very general and fragmentary character of much of our work. We hope if possible in the future to make further studies in this most fascinating field of chemical research.

In conclusion the writer desires to acknowledge the help and encouragement received from various friends. Our thanks are

due to Dr. W. Frear of this experiment station for advice and suggestions in the preparation of these papers; to Dr. G. G. Pond of the Pennsylvania State College for the use of a refractometer, and to Dr. F. E. Tuttle of the same institution for assistance in making combustions; also to Mr. C. W. Norris of this experiment station, who made many of the determinations of specific gravity and melting-point contained in the tables of these articles, and who also rendered valuable assistance in determining calories of combustion. We also wish to express our indebtedness to Messrs. A. N. Diehl and C. P. Beistle of this station for their kindly aid at various stages of the laboratory work.

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SOME BOILING-POINT CURVES.

PAPER II.

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In a recent paper on boiling-point curves[1] I presented the results of my work on mixtures of organic liquids in which alcohol, acetone and chloroform respectively was one of the constituents. In the following paper I have worked out the curves for mixtures in which benzene and methyl alcohol, respectively, is one of the constituents.

The apparatus and thermometer used were the same as those employed in my previous work and, therefore, need no description. All of the chemicals used were purified as I have already described, with the addition of benzene, which was first allowed to stand over sulphuric acid to both dry and remove any possible traces of thiophene and then decanted and distilled through a high column. None of the purified materials varied more than 0.5° C. in their boiling-point and nearly all not more than 0.1° C.

All readings were made at the prevailing atmospheric pressure and in no case was the variation great enough to seriously affect the accuracy of the results. For purposes of comparison the curve for benzene and alcohol by Thayer,[2] for benzene and carbon

[1] *J. Phys. Chem.*, **3**, 317 (1899).

[2] *Ibid.*, **2**, 382 (1898).

disulphide by Carveth,[1] for methyl alcohol and acetone and methyl alcohol and chloroform by myself, are included.

Following are the analytical data and charts, in which the temperatures are plotted as ordinates and the percentage compositions by weight as abscissas:

BENZENE AND CHLOROFORM.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.3	761.5	45.2	72.65	761.5
85.1	78.85	761.5	40.5	71.7	761.4
70.4	76.9°	761.5	34.1	70.35	761.4
61.9	75.65	761.5	27.7	68.9	761.4
55.9	74.6	761.5	18.8	66.7	761.4
52.0	73.9°	761.5	8.2	63.9	761.4
47.3	73.025	761.4	0.0	61.6	761.4

BENZENE AND CARBON TETRACHLORIDE.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.35	763.1	45.5	78.3	763.6
82.1	79.8	763.1	40.2	78.1	763.6
73.5	79.4	763.1	35.2	77.9	763.6
66.1	79.15	763.1	28.6	77.65	763.6
59.4	78.9	763.0	19.7	77.35	763.6
51.9	78.6	763.0	10.7	77.1	763.6
47.7	78.4	763.0	0.0	76.925	763.7

BENZENE AND ETHER.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.3	762.9	46.4	47.8	760.7
83.2	67.5	762.9	41.4	46.1	760.7
72.8	60.65	762.9	36.0	44.35	760.8
64.3	55.95	762.7	29.3	42.3	760.9
56.1	52.0	762.4	14.4	38.15	761.0
51.4	50.05	762.0	0.0	34.75	761.1
47.4	48.5	762.0	....	....	....

BENZENE AND ACETONE.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.5	767.2	49.8	62.0	766.5
87.1	72.2	767.1	47.2	61.6	766.5
78.2	68.55	767.0	41.1	60.75	766.6
68.9	65.85	76.70	33.6	59.8	766.6
60.2	63.9	76.70	23.8	58.75	766.6
54.3	62.8	767.0	9.9	57.5	766.6
50.3	62.1	767.0	0.0	56.7	766.7

[1] *J. Phys. Chem.*, **3**, 193 (1899).

Benzene and Methyl Alcohol.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.25	760.8	56.8	58.3	760.5
92.7	60.95	760.8	51.4	58.4	760.5
89.7	59.85	760.8	49.3	58.42	760.4
87.5	59.4	760.8	46.8	58.45	759.5
83.4	58.92	760.8	42.5	58.6	759.5
81.2	58.8	760.8	35.3	59.0	759.6
76.2	58.525	760.8	26.3	59.8	759.7
73.9	58.475	760.8	16.5	61.2	759.8
69.7	58.4	760.8	6.9	63.2	759.8
65.7	58.3	760.8	0.0	65.0	759.9
61.8	58.3	760.7	....	....	....

Methyl Alcohol and Ethyl Alcohol.

Per cent. methyl alcohol.	Temperature.	Barometer.	Per cent. methyl alcohol.	Temperature.	Barometer.
100.	65.1	762.7	46.0	70.65	762.5
88.1	66.1	762.7	42.4	71.15	762.5
74.6	67.35	762.7	36.5	72.0	762.5
65.4	68.3	762.7	24.9	73.9	762.5
55.9	69.4	762.7	11.1	76.5	762.5
50.0	70.1	762.7	0.0	78.75	762.5
46.2	70.6	762.7	....	....	....

Methyl Alcohol and Carbon Tetrachloride.

Per cent. methyl alcohol.	Temperature.	Barometer.	Per cent. methyl alcohol.	Temperature.	Barometer.
100.	65.2	765.1	40.6	56.6	765.3
93.9	64.0	765.1	38.5	56.475	765.5
87.2	62.7	765.1	31.8	56.2	765.5
75.0	60.5	765.2	24.9	56.0	765.5
64.0	58.85	765.2	20.7	55.97	765.5
59.6	58.3	765.3	18.4	55.95	765.5
54.9	57.8	765.3	15.0	56.0	765.5
51.6	57.45	765.4	11.1	56.1	765.3
48.6	57.2	765.4	7.4	56.35	765.3
45.6	56 9	765.4	5.9	56.6	765.3
42.1	56.7	765.4	0.0	77.2	765.3

Methyl Alcohol and Ether.

Per cent. methyl alcohol.	Temperature.	Barometer.	Per cent. methyl alcohol.	Temperature.	Barometer.
100.	65.15	765.3	39.1	40.1	765.3
85.3	57.7	765.3	36.5	39.55	765.3
70.4	50.2	765.3	36.2	39.42	765.1
63.1	47.1	765.3	30.7	38.5	765.1
56.2	44.7	765.3	18.4	36.6	765.1
49.7	42.7	765.3	0.0	34.85	765.1
44.5	41.4	765.3	....	....	....

Chart I represents the results obtained in mixtures where benzene was one constituent. The curve for carbon tetrachloride has already been worked out by Lehfelt,[1] by measuring the vapor-pressure with varying composition, the temperature being kept constant. Since it rested on so few measurements, however, I have thought it worth while to repeat his work. The results obtained were very much the same as those already given by Lehfelt. The curve has no maximum or minimum point and presents no unusual features other than the absence of such a point when the boiling-point of the constituents lie so close together.

The curves for chloroform, acetone, carbon disulphide and ether have neither maximum nor minimum point and present no unusual features. The curve for methyl alcohol, like that for ethyl alcohol, has a minimum point at about 58.3° C. Owing to the flatness of the curve at this point, however, the exact composition of the constant boiling mixture can not be given from my work. We can only say that it lies somewhere between 53 and 67 per cent. of benzene. The methyl alcohol curve cuts the ether curve at a composition of about sixty-nine per cent. benzene, the carbon disulphide curve at a composition of about fifty-five per cent. benzene, the acetone curve at a composition of about thirty-one per cent. benzene, and the chloroform curve at a composition of about six per cent. benzene.

In Chart II the results are given for mixtures of the various liquids with methyl alcohol. The curve for ethyl alcohol has neither maximum nor minimum point, which we might expect since the boiling-points of these two liquids are rather close together. But, here again, as in the carbon tetrachloride and chloroform curve, presented in my first paper, the close chemical relationship of these two compounds may be a strong modifying influence.

The curve for benzene has a minimum point at about 58.3° C. and a composition of fifty-three to sixty-seven per cent. benzene. The curve for carbon tetrachloride has a minimum point at about 55.95° C. and a composition of 18.4 per cent. methyl alcohol. The curve for ether has neither maximum nor minimum point and presents no unusual features. The curves for chloroform

[1] *Phil. Mag.*, and *J. of Science*, **46**, No. 278 (1898).

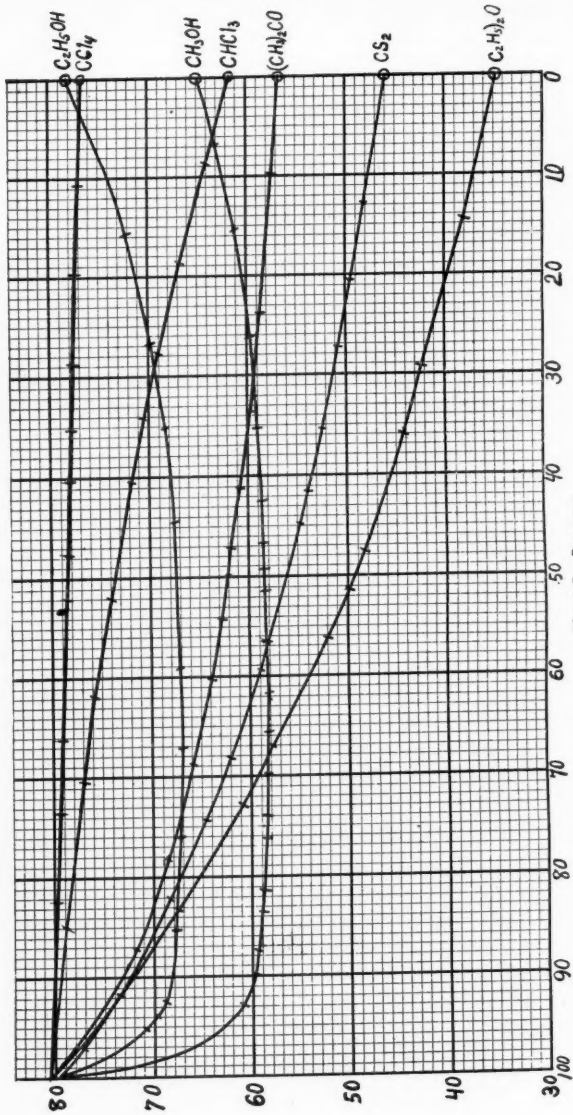

Chart I.—Benzene.

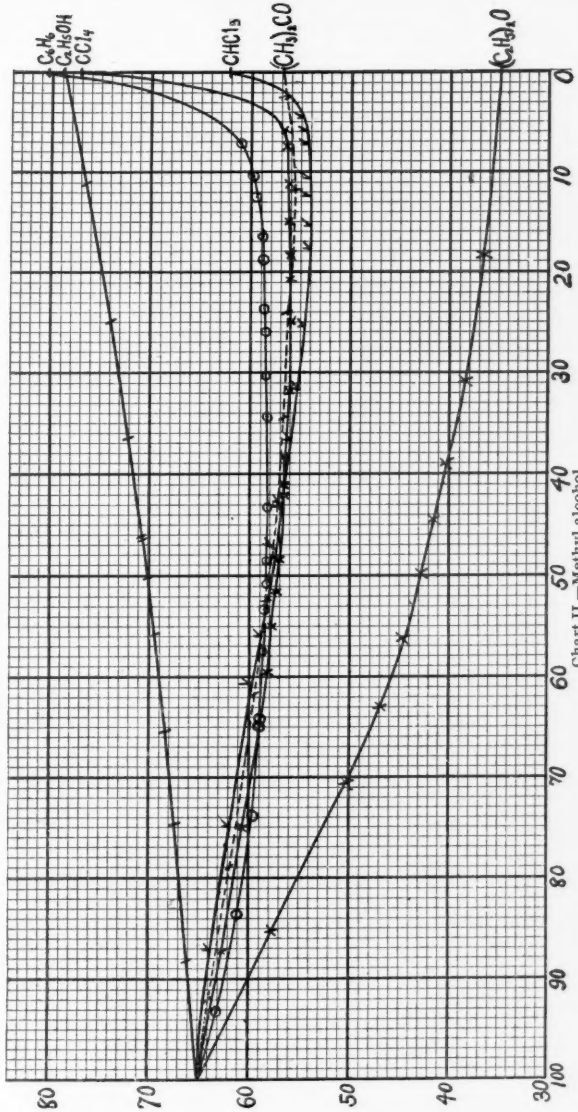

Chart II.—Methyl alcohol.

and carbon tetrachloride respectively both have minimum points, but need no further mention, as they have been fully discussed in my first paper.

If now the above chart representing the curves for methyl alcohol, is compared with the chart in paper I representing the curves for ethyl alcohol, it will at once be seen that the curves for the several liquids with methyl alcohol are quite similar to the curves for the same liquids with ethyl alcohol, each to each. Thus, the statement made in paper I, "In general, one constituent remaining the same, mixtures with substances of similar chemical constitution yield similar boiling-point curves," is borne out. The only exception one might pick out in these two sets of curves is when the methyl alcohol and acetone curve and the ethyl alcohol and acetone curve are compared. The first of these has a minimum point and the second has not. Granting, however, that this is the case, the minimum point of the methyl alcohol and acetone curve is only 0.8° C. below the boiling-point of the pure acetone, and the general shape of the curve is exactly the same as that of the ethyl alcohol and acetone curve.

From the data here presented the following conclusions may be drawn:

1. All mixtures of the following pairs of liquids boil at temperatures between the boiling-points of the constituents: Benzene and chloroform, benzene and carbon tetrachloride, benzene and ether, benzene and acetone, methyl alcohol, ethyl alcohol, and methyl alcohol and ether.

2. A solution containing 33 to 47 per cent. methyl alcohol in benzene distils without change at about 58.3° C. under a pressure of 760.7 mm. of mercury.

3. A solution containing about 18.4 per cent. methyl alcohol in carbon tetrachloride distils without change at 55.95° C. approximately under a pressure of 765.5 mm. of mercury.

4. The statement of paper I is borne out that "In general one constituent remaining the same, mixtures with substances of similar chemical constitution yield similar boiling-point curves."

5. Further, the statement in paper I is also borne out that: "The close proximity of the boiling-points of the constituents appears to be a favorable condition for the existence of a maximum or a minimum point on the boiling-point curve,

similarity of constituents seems to be a strongly modifying condition however.

Note.—Since sending the above article to press I am in receipt of a reprint of a paper entitled, "A Contribution to the Study of Liquid Mixtures of Constant Boiling-point," by Dr. Garnett Ryland,[1] in which are described his investigations of some of the same mixtures as are given in the above paper and paper I. They are benzene and chloroform, benzene and methyl alcohol, methyl alcohol and ether, methyl alcohol and acetone, and methyl alcohol and chloroform. His results are in the main the same as those obtained by myself, except in the case of methyl alcohol and acetone. He finds that this mixture can be separated by fractional distillation, while I find that the mixture has a minimum point about 0.8° C. below the boiling-point of the pure solvent.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 49.]

THE ELECTROLYSIS OF METALLIC PHOSPHATE SOLUTIONS.

BY HARRY M. FERNBERGER AND EDGAR F. SMITH.

Received August 2, 1899.

THE action of the current upon metallic phosphates, has received considerable attention in this laboratory. The frequent satisfactory repetition of these methods has only served to convince us that they deserve a permanent place in electrolytic literature, hence we take the present opportunity of again calling attention to them in their modified forms as to current density, voltage, etc., factors which were not especially emphasized in the earlier communications. Furthermore, other interesting behaviors of various metals in phosphate solutions, having come to light, we shall include them here. They are at least suggestive.

COPPER.

To a solution of copper sulphate, equivalent to 0.1239 gram of metal, were added twenty cc. of disodium hydrogen phosphate (sp. gr. 1.0358), and the precipitate produced was dissolved in five cc. of phosphoric acid (sp. gr. 1.347). The electrolytic

[1] Dissertation, Johns Hopkins University, 1898.

decomposition was then made with the following prevailing conditions:

$N.D._{100}$	0.035 to 0.068 ampere.
Voltage	2.2 to 2.6.
Dilution	225 cc.
Temperature	54°–64°.
Time	6 to 7 hours.

The deposit of copper weighed 0.1244 gram. It showed a deep red color. The metal could not be detected in the filtrate. A second trial gave 0.1243 gram of copper.

COPPER FROM IRON.

Sixty cc. of a disodium hydrogen phosphate solution (sp. gr. 1.0358) were added to twenty-five cc. of a copper sulphate solution (= 0.1239 gram of copper) and fifty cc. of a ferric ammonium sulphate solution (= 0.2002 gram of iron). The resulting precipitate was dissolved in ten cc. of phosphoric acid (sp. gr. 1.347). The conditions existing during the electrolysis were:

$N.D._{100}$	0.04 ampere.
Voltage	2.4.
Dilution	225 cc.
Temperature	53° C.
Time	7 hours.

The copper deposit weighed 0.1237 gram. Its color was brown-red, and it showed a silky luster. Iron was not found in it. The filtrate contained no copper.

COPPER FROM ALUMINUM.

To a solution containing 0.1239 gram of copper and 0.1000 gram of aluminum, were added sixty cc. of disodium hydrogen phosphate (sp. gr. 1.0338) and five cc. of phosphoric acid (sp. gr. 1.347). The conditions were:

$N.D._{100}$	0.068 ampere.
Voltage	2.6.
Dilution	225 cc.
Temperature	77°.
Time	6 hours.

The precipitated copper weighed 0.1240 gram. It was not contaminated with aluminum, nor did the filtrate show any signs of copper.

COPPER FROM CHROMIUM.

Sixty cc. of disodium hydrogen phosphate (sp. gr. 1.033) and 8 cc. of phosphoric acid (sp. gr. 1.347) were added to a solution containing 0.1239 gram of metallic copper and 0.1403 gram of chromium. The precipitation of metal then occurred with the following conditions:

$N.D._{100}$	0.062 ampere.
Voltage	2.5.
Dilution	225 cc.
Temperature	64°.
Time	6 hours.

The deposit of copper weighed 0.1243 gram. The filtrate did not show the presence of copper, nor could chromium be detected in the precipitated metal.

When the conditions given in the preceding separations are observed there need be no doubt as to the results.

COPPER FROM COBALT.

Sixty cc. of disodium hydrogen phosphate, and ten cc. of phosphoric acid were added to a liquid containing 0.1239 gram of metallic copper and 0.1000 gram of metallic cobalt. It was then electrolyzed with:

$N.D._{100}$	0.035 ampere.
Voltage	1.5.
Dilution	225 cc.
Temperature	62°.
Time	6 hours.

The precipitated copper weighed 0.1243 gram. It did not contain cobalt.

COPPER FROM ZINC.

Salts of these two metals, containing the same quantities of disodium hydrogen phosphate and phosphoric acid, were electrolyzed with:

$N.D._{100}$	0.035 ampere.
Voltage	2.5.
Dilution	225 cc.
Temperature	60°.
Time	5 hours.

The copper weighed 0.1244 gram, and was free from zinc.

COPPER FROM NICKEL.

A solution of copper sulphate (= 0.1239 gram of copper) and nickel nitrate (= 0.1366 gram of nickel) was mixed with seventy-five cc. of disodium hydrogen phosphate (sp. gr. 1.033) and ten cc. of phosphoric acid (sp. gr. 1.347). The conditions of electrolysis were:

$N.D_{100}$	0.072 ampere.
Voltage	2.45.
Dilution	225 cc.
Temperature	66° C.
Time	6 hours.

The precipitated copper weighed 0.1241 gram. The filtrate did not show the presence of this metal, and the deposit was free from nickel.

It was thought advisable to carry out the separation of copper in phosphate solution, not from a single metal alone, but from several, and note the most favorable conditions.

COPPER FROM IRON, COBALT, AND ZINC.

The solution contained 0.1239 gram of copper, 0.1007 gram of cobalt, 0.1000 gram of iron, thirty cc. of disodium hydrogen phosphate (sp. gr. 1.0358), and fifteen cc. of phosphoric acid (sp. gr. 1.347). The conditions of the electrolysis were:

$N.D._{100}$	0.04 to 0.05 ampere.
Voltage	2.3.
Dilution	225 cc.
Temperature	57°.
Time	6 hours.

The deposit of copper weighed 0.1240 gram. It was free from the other metals.

COPPER FROM MANGANESE.

A solution containing about equal amounts of the two metals together with sixty cc. of disodium hydrogen phosphate (sp. gr. 1.038) and ten cc. of phosphoric acid (sp. gr. 1.347), was electrolyzed with:

$N.D._{100}$	0.05 ampere.
Voltage	2.5.
Dilution	225 cc.
Temperature	56° C.
Time	6 hours.

The copper deposit weighed 0.1236 gram. The preceding determinations were all conducted with comparatively feeble currents.

Trials were made with stronger currents with several of the metals.

NICKEL.

Thirty cc. of disodium hydrogen phosphate were added to a nickel solution (= 0.070 gram of nickel), and the resulting precipitate was then dissolved in just sufficient phosphoric acid (1.347 sp. gr.) for that purpose, with several drops in excess. The electrolysis was then made with:

$N.D._{100}$	0.50 ampere.
Voltage	7–8.
Dilution	225 cc.
Temperature	68° C.
Time	3½ hours.

The precipitate of nickel weighed 0.0703 gram. The filtrate was found free from that metal. A second nickel solution (= 0.1360 gram of metal), forty-five cc. of disodium hydrogen phosphate (sp. gr. 1.038) and phosphoric acid (sp. gr. 1.347) sufficient to dissolve the precipitate, with a few drops in excess, was electrolyzed with:

$N.D._{100}$	0.53 ampere.
Voltage	7.
Dilution	225 cc.
Temperature	65°.
Time	3½ hours.

The nickel precipitate weighed 0.1360 gram. These deposits of nickel were dull gray in color, resembling the appearance to some extent of the platinum dish. They were very adherent, and were readily handled and washed. Notwithstanding the precipitation of the metal was complete, the attempts to separate it in this way from manganese and chromium were fruitless. On examining the deposit from the nickel and manganese solution it was found to contain phosphorus.

The use of stronger currents with zinc salts failed to give satisfactory results. A qualitative test made with cobalt seemed to indicate that this metal could be deposited with conditions similar to those used with nickel. A solution, containing both

iron and manganese, was also acted upon with a current similar to that employed with nickel and cobalt but neither of the metals was deposited. We were equally unsuccessful in depositing uranium from an acid phosphate solution.

MERCURY.

Twenty-five cc. of a mercuric chloride solution (= 0.1159 gram of metal), thirty cc. of disodium hydrogen phosphate (sp. gr. 1.038) and five cc. of phosphoric acid (sp. gr. 1.347), were electrolyzed with :

$N.D._{100}$	0.04 ampere.
Voltage	1.6.
Dilution	175 cc.
Temperature	50° C.
Time	4 hours.

The precipitated mercury weighed 0.1162 gram. It was silvery white in color and drop-like in appearance.

MERCURY FROM ZINC.

Twenty-five cc. of a mercuric chloride solution (= 0.1159 gram of metal), twenty-five cc. of zinc sulphate (= 0.1010 gram of zinc), sixty cc. of disodium hydrogen phosphate (sp. gr. = 1.038) and ten cc. of phosphoric acid (sp. gr. = 1.347), were electrolyzed with :

$N.D._{100}$	0.01 ampere.
Voltage	1.5.
Dilution	175 cc.
Temperature	60° C.
Time	4–5 hours.

The deposit of mercury weighed 0.1163 gram. It was free from zinc. The filtrate did not show any mercury.

The separation of mercury from cadmium did not succeed. As uranium was not precipitated under similar conditions we hoped for a separation of this metal from mercury and also from copper.

MERCURY FROM URANIUM.

A solution containing 0.1159 gram of mercury, 0.1018 gram of uranium, sixty cc. of disodium hydrogen phosphate (sp. gr. 1.038), and ten cc. of phosphoric acid (sp. gr. 1.347), was electrolyzed with :

$N.D._{100}$	0.017 amperes.
Voltage	2.45.
Dilution	175 cc.
Temperature	61° C.
Time	5½ hours.

The deposit weighed 0.2370 gram. It was heavier, therefore, than the combined weights of the mercury and uranium. A second trial was made after increasing the volume of phosphoric acid to fifteen cc. The deposit weighed 0.2012 gram. It had a dull lead color. It was strongly ignited to expel the mercury. The scaly residue was boiled with dilute nitric acid and the solution tested with ammonium molybdate. Large amounts of phosphorus were indicated. This would prove that the original deposits of metallic mercury so influenced the uranium salts that they were coprecipitated with that metal. Whatever the composition of the deposit may be it is certainly very variable. It is quite probable that a hydrous uranium phosphate is deposited with the mercury. The filtrates were all free from uranium.

On trying to effect the separation of copper from uranium in acid phosphate solution we experienced the same difficulty as with mercury and uranium. The precipitate consisted of copper, uranium, and phosphorus. The filtrate showed no signs of either copper or uranium. The separation of mercury and manganese was far from satisfactory. The same must be said of nickel and cobalt. They were partially precipitated with the mercury and carried down phosphorus with them. A qualitative test was made to separate uranium in the presence of mercury and phosphoric acid, electrolytically from iron. The deposit contained no iron when a current of $N.D._{100} = 0.006$ ampere was employed. This separation will receive further study in the immediate future.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 50.]

OBSERVATIONS UPON TUNGSTEN.

BY EDGAR F. SMITH.

Received August 5, 1899.

THIS communication presents fragmentary data upon tungsten collected during a period of years and amply verified by repeated reviews. As tungsten in its various combinations has been an object of great interest to the writer, particularly

the question as to its atomic mass, it need not surprise the reader to find that recourse has been had to so many diverse derivatives in the search for some body which would possess a constitution and properties suitable for an investigation of the problem. In the course of the study numerous observations were made which are not wholly devoid of interest and which are now incorporated in the following paragraphs. The solubility of tungsten trioxide and its derivatives in sulphur chloride deserves consideration; as do the facts that the third oxygen atom defies removal in this way and that pure sulphur chloride does not attack metallic tungsten, hereby enabling us to eliminate the final traces of oxides. The great volatility of the trioxide, on exposure to heat, condemns the ignition of metal in air as a means of deriving the atomic mass. Then, too, the establishment of a crystalline oxide is of some moment. Why the alkyl derivatives failed to appear is difficult to understand. If they could be prepared they would, doubtless, afford a splendid means of determining the atomic mass. Perhaps in the near future we shall find some method of making them. However, it is possible that the more metallic nature of tungsten will prohibit the formation of stable alkyls as seems obvious with the esters of tungstic acid.

For the experimental part of the work the writer is indebted to the several gentlemen whose names are given in the proper places and would here return them his sincere thanks for their kind and indispensable assistance.

I. The Action of Sulphur Monochloride upon Tungsten Trioxide.

By Hermann Fleck.

Attention has been directed to the action of sulphur monochloride upon various natural sulphides and oxides.[1] The purpose, primarily, of my study was to ascertain the nature of the body produced when tungsten trioxide, or any of its naturally occurring combinations, *e. g.*, wolframite or scheelite, were heated together with sulphur monochloride to 145° C. On cooling scarlet-red, prismatic needles, one of which measured two and one-half inches, crystallized from the red solution. On exposure to the air they immediately decomposed, evolving hydrochloric

[1] This Journal, 20, 289.

acid, and changing to tungsten trioxide. They dissolved freely in carbon disulphide and sulphur monochloride, but sparingly in benzene. The first crops were impure and gave very unsatisfactory analytical results. To eliminate a yellow powdery substance, admixed with the crystals, the following course was pursued: a tube containing the scarlet crystals, yellow powder, and mother-liquor from which the pressure had been released, was resealed and placed in an upright position in a tall beaker containing boiling water. The sulphur chloride became blood-red in color due to the dissolved crystals. The tube was now carefully inclined and the liquid drained away from the heavy yellow substance into the other end of the tube. The solution cooled instantly and a nest of beautiful crystals separated from it. This procedure was repeated until a complete separation of the two bodies had been achieved. Having finally removed the scarlet crystals from the tube they were further purified by sublimation and recrystallization from suitable solvents. With proper care and exclusion of moisture both courses yielded satisfactory results.

In the sublimation process five to ten grams of the crystals were placed in a wider tube with a three-holed stopper, carrying an inlet and exit tube as usual and a thermometer. The apparatus was filled with perfectly dry carbon dioxide and heat applied. First a ring of condensed mother-liquor made its appearance. The red crystals became dark in color and began to boil at 215°. The volatilization was complete at 225°. By careful fractional sublimation into bulbs filled with carbon dioxide magnificent scarlet crystals were obtained. These were analyzed. They showed the presence of 53.53 per cent., 53.59 per cent. and 53.94 per cent. of tungsten with 40.99 per cent. of chlorine; no sulphur was found. The oxychloride of tungsten ($WOCl_4$) required 53.94 per cent. of tungsten and 41.38 per cent. of chlorine.

The product of the interaction of sulphur monochloride and tungsten trioxide is, therefore, tungsten oxytetrachloride—$WOCl_4$. Again, a large mass of crystals after removal from the tube was quickly pressed between paper and recrystallized from small quantities of sulphur chloride with which it was boiled and subsequently allowed to cool in an Erlenmeyer flask. After

being freed in this way from the mother-liquor containing sulphur, they were washed with carbon disulphide previously dehydrated by standing over sodium wire. The adhering carbon disulphide was expelled in a current of dry carbon dioxide and the flask was then tightly stoppered. The flask and contents were weighed and a portion of the material removed, after which the flask was reweighed. The quantity of substance for analysis was thus found by difference. The analysis showed the presence of 35.51 per cent. of tungsten and 39.5 per cent. of chlorine. When it is considered that over seven grams of material were used in the estimation of the tungsten, eleven grams for the chlorine and even a larger quantity for the sulphur, the results will not fail to win favor. That the chlorine content is low is not astonishing if we recall how tenaciously moist tungsten trioxide retains hydrochloric and sulphuric acids.

These analytical results and the boiling-point of the scarlet crystals, establish their identity as tungsten oxychloride.

Tungsten dioxide was also changed to the same body on heating it with sulphur monochloride. Even when the oxides were exposed with the sulphur chloride to temperatures as high as 240°, the third oxygen atom was not displaced. Tungsten hexachloride and tungsten dioxychloride were never observed.

The action of sulphur chloride upon tungsten metal was also tried. The result of this study showed that pure sulphur chloride, free from chlorine, has no action upon the metal, but when that gas is present in sufficient quantity the metal can be completely changed to the hexachloride, crytallizing in steel-blue needles and forming dark red vapors. With an insufficiency of chlorine, black crystals are produced. These were found to be hexachloride contaminated with metallic tungsten.

Finely divided wolframite and scheelite, as already noted, are also soluble in sulphur monochloride. It may be added that this method affords an excellent means of preparing the red oxychloride. Indeed, it seems to be a superior method in every way for that purpose.

I shall now return to an observation noted in the first section of this communication; *viz.*, that tungsten trioxide used in atomic mass work did not entirely dissolve in sulphur chloride when heated to 145° C. Further, it was always necessary to free the

oxychloride from adherent trioxide. Why, if this be pure oxide of tungsten, does it not dissolve completely? Can it be that this insoluble part is the impurity in the oxide which affects the atomic mass? Is it perhaps a nitride, or oxynitride, or some allotropic modification of the trioxide? These questions suggested themselves from time to time and efforts were made to answer them. How this was done will appear in the following paragraphs:

1. Two grams of tungsten trioxide, made from ammonium tungstate, were heated to 145° with sulphur monochloride. On cooling the red crystals separated from the solution, leaving, however, much unattacked original material. The crystals were roughly separated from the deposit, pressed between folds of filter-paper, and then allowed to decompose in the air. They were moistened, ignited to the trioxide and reheated in a sealed tube with sulphur monochloride. This trioxide disappeared almost entirely at 140°–170°, yielding the red crystals as before. The portion remaining unattacked was washed with carbon disulphide, dried, and ignited. It weighed six-tenths gram. When reheated with sulphur monochloride at 140°–170° it did not dissolve. Larger quantities of ignited tungsten trioxide were treated in this way and thus separated into two distinct parts, each of which was exposed to the action of sulphur chloride until it ceased to dissolve any more. From 150°–180° there was no further action on the insoluble portion. This point is also indicated by the sulphur chloride no longer assuming a red color due to the oxychloride which it may contain. The oxide from the red crystals, when decomposed and ignited, left a portion of substance insoluble in sulphur monochloride. Could it be that in the ignition of this oxide there was something abstracted from the air that rendered it insoluble in sulphur monochloride? If this were true then it could be readily understood why the oxide prepared by the ignition of ammonium tungstate was so largely insoluble in the sulphur chloride. It would also account for some of the discrepancies noticed in the atomic mass determinations.

2. To demonstrate that the trioxide changes either to an allotropic modification or to some other body, by ignition in air, a sample of it was made by heating moistened oxychloride as gen-

tly as possible. It was then divided into two equal portions (*a* and *b*) of one gram each in weight.

a was placed directly into a tube with S_2Cl_2 and heated for eight hours from 150°-170°.

b was *not* placed directly into a tube but was heated alone for eight hours in air at a high temperature and then exposed for eight hours to the action of sulphur chloride at 150°–170°.

The contents of *a* were completely dissolved, whereas those of *b* were unattacked. The question remained—what is this insoluble substance?

3. All the material which had previously proved insoluble in sulphur chloride was now collected and heated with this reagent in sealed tubes to 250°. *Its solution was complete.*

4. Possibly the insoluble compound represented an oxynitride. I thought this might be ascertained by analyzing the air in which the trioxide was ignited or by proving the presence of nitrogen in the insoluble material.

5. To demonstrate the falsity or correctness of the idea of an oxynitride having been produced, a portion of tungsten trioxide, soluble in sulphur chloride, was placed in a porcelain tube between two asbestos plugs. At one side was attached a reservoir, consisting of a wide tube, connected by rubber tubing to a second tube of about the same capacity. A regular Hempel burette and leveling tube were joined to the opposite end of the porcelain tube. Mercury was filled into the tubes and a definite volume of air into the burette, the oxygen of which had been accurately determined in another portion of it. Heat was applied to the tube and the air was passed back and forth over the trioxide by raising and lowering the leveling tubes alternately on both sides of the combustion tube. The heating process continued for three hours. After cooling the volume of air had not diminished. Neither nitrogen nor oxygen had been absorbed. *The oxide was not soluble in sulphur chloride.*

6. A portion of the "insoluble" material was placed in a hard glass tube and heated in an air current, which then passed into water, but no reaction for either nitric or nitrous acid was observed.

7. A tube of hard glass, sealed at one end and containing stick caustic potash, was attached to a vacuum pump and heated.

When it had melted and the gas particles enclosed in it had escaped, the tube was cooled and after the introduction of from ten to fifteen grams of the "insoluble" trioxide it was carefully exhausted and sealed. Its contents were heated, when the "insoluble" oxide disssolved. Any nitrogen that might have been present would have been expelled as such or in the form of ammonia. On opening the tube under mercury the latter filled it completely. Gases were not present.

II. Tungsten Alkyls.

By E. A. Barnett.

Riche[1] claims that when he heated metallic tungsten with methyl iodide to 240° in a sealed tube for ten days he obtained a product that upon distillation yielded unaltered methyl iodide and a viscous liquid. The latter only distilled at high temperatures. When it was shaken with a little warm ether-alcohol an oily substance separated, while the ethereal solution contained a compound melting at 110° and crystallizing in colorless plates. To this body he ascribed the formula $W(CH_3)_3I$. Cahours,[2] believing that the saturation power of W was WX_5, repeated the work and obtained the same body. I endeavored to prepare it with the purpose of making other alkyl derivatives in order to use the same in the redetermination of the atomic mass of tungsten. I heated one part of tungsten with four parts of methyl iodide for ten days to 240°. On opening the tubes a sharp, acid, unpleasant odor was noticed. The contents of the tubes were distilled out in a steam-bath. The distillate boiling at 42° proved to be methyl iodide. What remained in the tube was treated with ether-alcohol and filtered. The ether-alcohol solution was allowed to evaporate spontaneously; a greenish black mass remained but colorless crystals were not discernible. The residue was extracted with chloroform and this solution placed aside to crystallize. After standing awhile, plate-like forms appeared. These disclosed the presence of iodine upon applying the test. They also contained tungsten. Thus, 0.2765 gram of material yielded 0.2604 or 93.45 per cent. of tungsten. Two other determinations made with more care gave 94.38 per cent. and 94.31 per cent. of tungsten, respectively. Concentrated nitric acid,

[1] *Jsb. d. Chem.*, p. 373 (1856); *Compt. rend.*, **42**, 203 (1856); *J. prakt. Chem.*, **69**, 10.
[2] *Ann. Chem.* (Liebig), **122**, 70.

acting on the compound, liberated iodine vapors. The same was observed when heat was applied to the compound. Two determinations of the iodine content were made showing the presence of 1.18 per cent. and 1.58 per cent., respectively.

To ascertain whether the compound contained carbon, portions of it were carefully burnt in an air current, the gases being conducted into lime-water. A precipitate of calcium carbonate was produced. It was filtered out, and from its lime content the corresponding percentage of carbon was calculated. In this way were found 1.99 per cent. and 2.01 per cent. of carbon, respectively.

These results do not indicate a tungsten alkyl, but rather finely divided metal with carbon and adherent methyl iodide.

Tungsten hexachloride and mercury ethide were allowed to interact in ligroin solution. A dark blue mass resulted; this on standing became purplish black in color. I hoped that a change might occur in the sense of the equation:

$$6Hg(C_2H_5)_2 + WCl_6 = W(C_2H_5)_6 + 6Hg\begin{matrix}C_2H_5\\Cl\end{matrix}.$$

The reaction product was transferred to a filter and washed with cold ligroin, after which it was introduced into a Soxhlet apparatus and extracted with benzene for three hours. Its color was dark blue or purple. This was dried over sulphuric acid and analyzed:

	Tungsten. Per cent.	Chlorine. Per cent.
Found (in *a*)	46.33	9.55
" (in *b*)	46.27	9.21

Carbon was not present. Analyses of other portions revealed the presence of varying amounts of mercury and chlorine.

It is safe to conclude that an alkyl derivative of tungsten cannot be produced in this way. Indeed, I cannot help but doubt the existence of these bodies, for my experiments are not all which have been tried in this laboratory and which have resulted negatively. As little success has been had with molybdenum along similar lines.

III. Tungsten Alkyls.

By Clarence Hall.

It was my aim to prepare the alkyls of tungsten by the use of

zinc methide and a tungsten chloride. To this end I placed a bulb, containing three and seven-tenths grams of zinc methide, and another containing three and two-tenths grams of tungsten hexachloride in a glass tube sealed at the one end, while its other end was drawn out and through this contracted tube was passed a much smaller tube conveying dry nitrogen. This gas was allowed to pass for more than half an hour through the tube, after which the latter was sealed. By shaking it, the bulbs containing the zinc methide and tungsten hexachloride were broken. When their contents came together heat and light were produced and a black substance separated. After this the tube was heated for a period of six hours at a temperature of 70°. A decided pressure was noticed when the tube was opened. The tube contents were treated with ether and the solution examined for tungsten compounds. They were not found present. The residue showed the presence, on analysis, of tungsten, zinc, carbon, and hydrogen. The ratio of these constituents was indefinite. A second trial resulted similarly, so that I gave up all hope of preparing the alkyl body in this manner.

Thinking that possibly in the direct action of the alkylogens upon tungsten metal the character of the latter influenced the reaction, I concluded to act:

1. With methyl iodide upon tungsten obtained by passing sodium vapors in an atmosphere of hydrogen over gently ignited tungsten trioxide. The tube contents after exposure to 200° for from eight to ten days were treated and examined as indicated by Riche. The residue, on analysis, showed 1.71 per cent. of carbon, 91.33 per cent. of tungsten, 1.5 per cent. of iodine, and 0.34 per cent. of hydrogen.

2. The metal in this series of experiments was prepared by fusing tungsten hexachloride with metallic sodium. The resulting product was extracted with water and the tungsten was then further purified by alcohol and carefully dried. It was heated as before with methyl iodide. In this instance the alcohol-ether layer on evaporation left a white scaly substance which melted at 115°. It revealed the presence, on testing, of iodine, tungsten, and carbon. Had I really found Riche's compound? This I firmly believed until other experiments made in this lab-

oratory proved that this substance was nothing more than sodium iodide mixed with some ethereal tungsten body.

IV. Esters of Tungstic Acid.

By Claude Dugan.

Several chemists have recorded their experiences in preparing these compounds. Göessmann[1] endeavored to form them by allowing alkyl iodides to act upon silver tungstate, but was unsuccessful. Subsequently, Maly[2] obtained through the action of ethyl alcohol upon tungsten oxychloride ($WOCl_4$) a white flocculent precipitate, which after washing with alcohol was allowed to dry in the air and later over sulphuric acid, when it became a hard, brittle vitreous mass. A single analysis of it gave 85.16 per cent. of tungsten, 5 per cent. of carbon, and 1.64 per cent. of hydrogen, pointing, in the judgment of Maly, to an ester of metatungstic acid, $W_2O_6.H.C_2H_5 + H_2O$.

I repeated this experiment, obtaining a body which revealed the presence of 79.6 per cent. of tungsten, 1.06 per cent. of carbon, and 0.84 per cent. of hydrogen.

Not doubting in the least the observation of Maly, but thinking probably that the reaction or transposition was not as simple as might be inferred upon reading his paper and that by the action of the hydrochloric acid, evolved in the change, upon the unconsumed alcohol present, water would be produced and this in turn would form varying amounts of tungstic acid which naturally would contaminate the resulting ester, I studied the action of other alcohols in a pure and dry state upon beautifully crystallized and purified tungsten oxychloride.

First, let me present my experience with isobutyl alcohol in the line indicated. When it and the oxychloride were brought together much heat was evolved; a yellow precipitate separated after standing. The filtrate from this was distilled under reduced pressure, when a white starchy mass appeared. This was dried over phosphorus pentoxide and soda-lime. When nearly dry it was dissolved in anhydrous ether. To the ethereal solution pure anhydrous ethyl alcohol was added with the production of a gelatinous white precipitate which was collected and carefully handled until dry and ready for analysis. It was

[1] *Ann. Chem.* (Liebig), 101, 218.

[2] *Ibid.*, 139, 240.

a very brittle powder and contained 7.4 per cent. of carbon, 1.60 per cent. of hydrogen, 65.00 per cent. of tungsten, and 5.76 per cent. of chlorine, which closely approximate the requirements of a compound of the formula

$$3WO_3.2H_2O + WOCl_2(O.C_4H_9)_2.$$

In other words the transposition between the oxychloride and the alcohol was not complete and to the new product there was added hydrated tungstic acid. Whether it is possible to effect a complete transformation and whether the ester can be isolated without contamination with tungstic acid, appears to me rather doubtful. I am led to this view because upon substituting other alcohols and proceeding in the manner of Maly, I invariably obtained products of complex character, containing tungsten, carbon, hydrogen and chlorine. Thus with propyl alcohol a product was isolated which showed the presence of 10.3 per cent. of carbon, 4 per cent. of hydrogen, 6.3 per cent. of tungsten and 5.32 per cent. of chlorine. With amyl alcohol the case was practically the same, and it seems evident that while esters of tungstic acid do perhaps exist they can only be isolated with extreme care and are surrounded by conditions which favor their ready and rapid breaking down. It must be admitted, however, that the tungstic acid in yielding these incomplete esters exhibits the character peculiar to the group in which it is placed by the periodic system and the instability of the desired and expected derivatives must be attributed to the absence of a sufficiently pronounced acid, or non-metallic, nature in the tungsten itself.

V. The Atomic Mass of Tungsten.

By Willett L. Hardin.

In an article published from this laboratory last year[1] it was demonstrated that the method usually employed in the determination of the atomic mass of tungsten is unsatisfactory. The results given in that paper were obtained by the reduction of tungsten trioxide in a current of hydrogen at a white heat, and the subsequent oxidation of the metal in air. Like the determinations of earlier experimenters, these results showed considerable variation; the maximum and minimum values for the atomic

[1] This Journal, 19, 657.

mass of tungsten differed as much as one and a half units. Some of the probable causes of these deviations were also discussed and certain sources of error pointed out.

It was proved, for example, that tungsten trioxide obtained from ammonium tungstate contains nitrogen; that the oxide of tungsten is slightly volatile or that a small portion is carried out mechanically by the water formed in the reduction; and also, that tungsten attacks the vessels in which the atomic mass determinations have been made.

The following experiments were undertaken in the hope of gathering further evidence as to the cause of these variations, and with a view of arriving at a more satisfactory conclusion in regard to the true atomic mass of tungsten.

Tungsten trioxide resulting from experiments made last year was heated to 145° in sulphur monochloride in a sealed tube. About 75 per cent. of the oxide was taken up by the sulphur chloride. When the solution cooled, red crystals separated; these were removed from the unattacked material and after washing with carbon bisulphide were ignited in a current of oxygen, and the oxide thus prepared was reduced in hydrogen.

	Tungsten trioxide. Grams.	Tungsten. Grams.	Atomic mass of tungsten.
1	2.42690	1.90610	175.68
2	1.62225	1.28195	180.80

The metal from these reductions was reoxidized:

Tungsten. Grams.	Tungsten trioxide. Grams.	Atomic mass of tungsten.
1.24369	1.56691	184.69

On reducing this oxide, the value 183.75 was obtained for the atomic mass of tungsten.

From these experiments it is obvious that the material produced by the ignition of the red crystals is not pure tungsten trioxide. A portion of it was reduced in hydrogen and the volatile products conducted through a solution of copper sulphate. A black precipitate of copper sulphide was thrown down, showing that the substance retained sulphur, even after it had been ignited in a current of oxygen.

When the metal from the red crystals was oxidized and the

product heated in sulphur monochloride in a sealed tube at a temperature of 145°, only a portion of it was taken up. This insoluble portion was supposed, at first, to contain nitrogen. A series of observations were made to decide this point.

The first experiment consisted in oxidizing the metal obtained from the red crystals in an atmosphere of commercial oxygen. This was carried out in an asbestos cell, the interior of which was covered with plaster of Paris. The crucible containing the metal was placed in an opening in the bottom of the cell, and a current of oxygen was introduced through a small glass tube which passed through the cover. This arrangement was used for a number of experiments but was unsatisfactory owing to the rapidity with which metallic tungsten oxidizes in an atmosphere of oxygen. The gas was taken up more rapidly than it could be supplied and consequently air passed into the cell around the sides of the crucible. In a second device the metal was oxidized in a combustion tube, the outlet of which was a long narrow tube, immersed at the lower end in mercury or sulphuric acid. This contrivance was very satisfactory in oxidizing the metal away from air.

The oxide obtained in this manner was more insoluble in sulphur monochloride than that obtained by the ignition of the metal in air.

The oxygen employed in these experiments, was then analyzed and found to contain six per cent. of nitrogen. An attempt was, therefore, made to obtain pure oxygen from potassium chlorate and manganese dioxide and from potassium chlorate alone. The gas was collected over recently-boiled distilled water. In every case the oxygen was found to contain about one per cent. of impurity, supposed to be nitrogen, but when tested was discovered to be carbon monoxide. The main object, however, was to get oxygen free from nitrogen; this was accomplished. Metallic tungsten was then oxidized in it, as already described, and the resulting oxide was found to be insoluble in sulphur monochloride at 145°.

The soluble and insoluble portions of oxide were next tested for nitrogen by reducing in hydrogen and conducting the resulting vapors into a dilute, standardized solution of hydrochloric acid. The strength of the acid was not perceptibly changed,

showing that not more than a trace of ammonia could have been formed.

The two portions of oxide were further tested for nitrogen by fusing with potassium hydroxide in a sealed glass tube which had been previously exhausted by means of a Geissler pump. The potassium hydroxide was fused before use and allowed to cool in a vacuum. After fusing the oxide with caustic potash, the contracted end of the tube was immersed in mercury and the tip broken off. The mercury completely filled the tube, showing that no gases had been set free in the reaction.

Atomic mass determinations were then made, using first the insoluble and afterward the soluble oxide. The trioxide, resulting from the ignition of the metal in air, was treated with sulphur monochloride at 145°. The insoluble portion was removed from the tube and reduced in a current of hydrogen. The resulting metal was oxidized in a current of oxygen and the following result obtained :

Tungsten. Grams.	Tungsten trioxide. Grams.	Atomic mass of tungsten.
2.68250	3.38144	184.20

The red crystals were then removed from the tube, heated in a current of oxygen and reduced in hydrogen. The resulting metal was oxidized as before :

Tungsten. Grams.	Tungsten trioxide. Grams.	Atomic mass of tungsten.
1.90428	2.40021	184.27

The two results are almost identical.

There appears then to be no difference in the composition of the soluble and insoluble oxides. The identity in their composition is also confirmed by the fact that one form can be converted into the other and *vice versa*. If the insoluble portion is converted into ammonium tungstate, the oxide resulting from the ignition of this salt is soluble in sulphur monochloride at 145°. When the metal obtained from the red crystals is oxidized in a current of oxygen, the resulting oxide is insoluble in sulphur chloride at 145°.

From these observations it seems that tungsten trioxide exists in two forms. To decide this point portions of the oxide were obtained by different methods, and carefully examined. One

portion of the material resulted from the oxidation of metallic tungsten in pure oxygen under a slightly increased pressure. An extremely high temperature was obtained by this procedure. Most of the oxide fused together in an opaque crystalline mass in the bottom of the boat, while a portion of it sublimed in beautiful, shining crystals on the sides of the boat. The fused mass seemed to be striated, indicating a prismatic structure. The sublimed crystals, however, appeared to be of a tetrahedral form. By strongly heating metallic tungsten in the air, Bernoulli[1] and Schafavik[2] obtained microscopic crystals of tungsten trioxide. By fusing the oxide with borax Nordenskjöld[3] also obtained small crystals. This is sufficient evidence to show that tungsten trioxide exists in two forms, the amorphous and crystalline. The latter form is produced from the former at high temperatures.

A sample of the oxide was then prepared by the ignition of ammonium tungstate in air, and another portion by the ignition of metallic tungsten in air. A series of specific gravity determinations were made, using these various samples of oxide. The results were as follows:

SPECIFIC GRAVITY OF TUNGSTEN TRIOXIDE.

Fused mass	7.502
Sublimed crystals	7.301
From ignition of tungsten in air	7.272
From ammonium tungstate	5.804
" " "	5.705
" " " (after high heating)	6.391
" " " (" " ")	6.820

These results leave no doubt as to the existence of two forms of tungsten trioxide. The specific gravity determinations of earlier experimenters point to the same conclusion:

Herapath	5.274
d' Elhujar	6.120
Karsten	7.130
Nordenskjöld	6.30–6.38
Zettnow	7.16–7.23

1 Pogg. *Ann.*, III, 595.
2 Sitzungsber. d. Akad. d. Wissenschaften in Wien.
3 Pogg. *Ann.*, 114, 246.

The determinations of Nordenskjöld were made with crystals obtained by fusing tungsten trioxide with borax. Under suitable conditions then, it seems that the yellow oxide of tungsten polymerizes.

DETERMINATION OF THE ATOMIC MASS OF TUNGSTEN BY THE OXIDATION OF THE METAL IN PURE OXYGEN.

After obtaining oxygen free from nitrogen, it was thought advisable to make use of this gas instead of air, in determining the atomic mass of tungsten by the oxidation method. The metallic tungsten was oxidized in a porcelain boat in a combustion tube. It was noticed in each experiment that a white sublimate was formed in the glass tube. The values obtained varied from 184.1 to 184.8. These results are of little value owing to the volatilization of the material.

An attempt was made to eliminate the error due to the volatilization of the oxide, by placing the boat containing the material in a glass tube, about twenty cm. in length, which had been drawn out to a small opening at one end. This tube together with the boat and contents was carefully weighed and placed in a larger combustion tube in which the oxidation was carried out. A sublimate was formed inside the smaller tube, and also on the walls of the combustion tube near the ends of the weighed tube. The results from these experiments are of no more value than those obtained without the use of the second tube.

A series of observations was next made to determine the amount of volatilization in the oxidation of a definite quantity of metallic tungsten. The same material was oxidized and reduced a number of times without being removed from the porcelain boat. The amount of volatilized oxide was not constant. The following results were obtained:

	Grams.
Weight of WO_3 at the beginning of the experiment..	2.36815
" " " after one reduction and reoxidation..	2.36780
" " " " two reductions and reoxidations	2.36560
" " " " three " " "	2.36430
" " " " four " " "	2.36401

Pure oxygen was used in these experiments. A sublimate was formed, however, when the metal was oxidized in air.

From these trials it is evident that no reliable atomic mass

determinations can be made by the oxidation of metallic tungsten either in air or in pure oxygen. The volatilization of substance would increase the values obtained for the atomic mass. No doubt this will explain why the results obtained by the oxidation method are, in general, higher than those obtained by the reduction method.[1]

OCCLUSION OF HYDROGEN BY METALLIC TUNGSTEN.

The occlusion of hydrogen by metallic tungsten has been suggested by some chemists as a probable source of error in the determination of the atomic mass of this element by the reduction and oxidation methods. Waddell[2] claims that no such occlusion occurs. Derenbach,[3] on the other hand, says that an appreciable quantity of hydrogen is retained by the finely divided metal. In the observations on the atomic mass of tungsten which were published from this laboratory last year, attention was called to the fact that the results obtained were the same whether the metal was cooled in an atmosphere of hydrogen or in a vacuum. In order to definitely settle this question the following experiments were made:

Metallic tungsten which had been allowed to cool in an atmosphere of hydrogen was oxidized in a current of carefully dried oxygen. The vapors resulting from the oxidation were conducted through a U-tube filled with glass wool and phosphorus pentoxide. The results of three experiments are as follows:

	Tungsten. Grams.	Water obtained. Gram.
1	2.5	0.00005
2	2.8	0.00070
3	3.0	0.00070

The quantity of hydrogen converted into water in these experiments is inappreciable in quantitative determinations.

In a second series of observations metallic tungsten was oxidized in a current of oxygen and the volatile products were collected over mercury, where they were carefully tested for hydrogen. The results were wholly negative. This precaution was taken owing to the fact that only a minute quantity of hydrogen was converted into water during the oxidation.

[1] See Pennington and Smith: *Ztschr. anorg. Chem.*, (1895).
[2] *Am. Chem. J.*, 8, 280 (1886).
[3] Thesis, Würzburg (1892).

From these and earlier experiments it is evident that no appreciable error in atomic mass determinations is introduced by the occlusion of hydrogen by the metallic tungsten.

EXPERIMENTS ON TUNGSTEN OXYCHLORIDE ($WOCl_4$).

The red crystals, resulting upon heating tungsten trioxide with sulphur monochloride in a sealed tube, were found to be the oxychloride. An attempt was made to determine the atomic mass of tungsten from analyses of this compound. The substance was removed from the sealed tube into a larger combustion tube, filled with carbon dioxide. It was then sublimed, in a current of carbon dioxide, into small glass bulbs which were afterward sealed off. The analysis was carried out in the following manner :

One of the bulbs containing a portion of the sublimed material was carefully weighed. The tip was then broken off and the bulb quickly introduced into a glass-stoppered distilling flask containing strong nitric acid. When the acid was heated the chlorine content of the crystals was changed to oxychlorides of nitrogen and free chlorine. These gases were expelled from the flask and collected over an aqueous solution of silver nitrate, previously saturated with silver chloride. The solution was contained in a long-necked, inverted flask. The vapors were allowed to remain in contact with the liquid until the chlorine was completely changed to silver chloride. The quantity of silver chloride formed was determined in the usual manner, using a Gooch crucible. All the washings were made with water containing a little nitric acid and saturated with silver chloride. The tungstic acid, which remained in the flask, was ignited and weighed as the trioxide.

A large series of analyses were made but the results were too discordant to establish anything with certainty. Upon careful examination it was discovered that the red crystals, even after sublimation, contained varying quantities of sulphur as an impurity. It was also found that the tungstic acid in the distilling flask retained chlorine. Traces of the latter could be detected in the oxide after ignition. In view of these difficulties the method was given up as valueless for atomic mass determinations.

PRECIPITATION OF SILVER BY MEANS OF METALLIC TUNGSTEN.

Smith[1] showed that silver could be precipitated as metal from an ammoniacal solution of the nitrate by means of metallic tungsten. The results proved that six atoms of silver were precipitated for each atom of tungsten added. Thinking that this method might prove of value in determining the atomic mass of tungsten quite a number of observations were made.

The silver used in the experiments was purified by the Stas method. The nitrate obtained from this metal was dissolved in pure water in a platinum dish; a slight excess of ammonium hydroxide was then added to the solution. Finely divided metallic tungsten was next added in sufficient quantity to precipitate about one-half of the silver present. The solution was digested for some time in the cold, and the quantity of silver, which had been precipitated, was then determined. Many of the results for the atomic mass of tungsten were close to the theoretical while others showed considerable variation. The quantity of ammonia in the solution was varied and experiments were made at different temperatures but the results were too variable to establish anything with certainty. The precipitated metallic silver was then carefully examined and found to contain small quantities of silver tungstate. Notwithstanding the presence of this substance, the results in many instances were close to the theoretical. The method, however, will not answer for atomic mass determinations.

EXPERIMENTS ON BARIUM METATUNGSTATE.

By estimating the water of crystallization in barium metatungstate, Scheibler[2] endeavored to determine the atomic mass of tungsten. His results varied more than one unit. The values from the determinations of barium and tungsten were rejected by him. In reviewing the work on tungsten, it was thought advisable to repeat these experiments.

The material was prepared in a manner similar to that described by Scheibler; sodium metatungstate was formed by boiling a solution of the normal salt with tungstic acid. The salt, which was obtained with difficulty by this method, was recrys-

[1] *Ztschr. anorg. Chem.*, **1**, 360 (1892).
[2] *J. prakt. Chem.*, **83**, 324 (1861).

tallized. Pure barium chloride was prepared by recrystallizing the commercial C. P. salt several times. Sodium metatungstate and barium chloride were then dissolved in water, heated to boiling and mixed in equivalent quantities. A portion of the tungsten and barium came down as a white precipitate; this was filtered out and the solution allowed to cool. During the cooling more of the white precipitate separated, and in many cases the whole tungsten content changed to the insoluble barium salt. In some instances, however, only a portion of the substance sustained this change. It was filtered out, and on further evaporation of the solution, crystals of barium metatungstate separated. In some of the preparations, the sodium metatungstate was made by the action of the electric current on the normal sodium salt. This material was furnished by Dr. Geo. E. Thomas.

The water content of the crystals was determined by heating the powdered salt in a porcelain crucible for one hour at a dull red heat. The results were varied. The salt appeared to be slightly efflorescent. The values obtained for the atomic mass of tungsten are more discordant than those obtained by Scheibler, and hence are of no particular value.

After decomposing the salt with aqua regia, the barium was determined as sulphate and the tungsten as trioxide. These results also varied too greatly for atomic mass determinations; they, however, approximated the generally accepted formula,

$$BaW_4O_{13} + 9H_2O.$$

THE MOST PROBABLE VALUE OF THE ATOMIC MASS OF TUNGSTEN.

It would appear that all of the preceding methods for the determination of the atomic mass of tungsten are unsatisfactory. So far as known, there is no perfectly reliable method for the determination of this constant. The method of reduction and oxidation is probably more accurate than any of the other methods which have been employed. The results obtained by it vary about one unit, and even more in exceptional cases. The high values published by some experimenters are undoubtedly due to the volatilization of oxide. The mean of all the determinations is approximately 184. Until a more accurate means

has been devised for determining the atomic mass of tungsten, it will perhaps be better to accept the result 184, as the most probable value of this constant.

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ON β-HEPTYLAMINE.[1,2]

[FIRST PAPER.]

BY THOMAS CLARKE.

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ALTHOUGH β-heptylamine has been prepared by Cahours and Pelouse[3] and later by Schorlemmer,[4] the description of it was so meager, that it was considered worth while to study this base more thoroughly.

β-Heptyl bromide, prepared according to the method of Venable[5] from heptane of the *Pinus sabiniana*, was heated in a sealed tube at 100° with an excess of an alcoholic solution of ammonia. The resulting products were primary β-heptylamine hydrobromide, ammonium bromide, heptylene, and unchanged β-heptyl bromide. There was no evidence of the formation of a base other than primary β-heptylamine, which accords with the observations of Jahn,[6] that by the action of ammonia on isopropyl iodide, β-hexyl iodide or β-octyl iodide, only amide bases are formed. The formation of unsaturated hydrocarbons of the series C_nH_{2n} was observed by Jahn,[7] in the action of ammonia on isopropyl iodide and β-hexyl iodide.

The results show that, similar to the examples cited from Jahn, two separate reactions take place in the action of ammonia on β-heptyl bromide. One is the condensation of the ammonia with the bromide to form the primary amine hydrobromide as shown in the following equation:

$$\begin{matrix} CH_3 \\ CH_3(CH_2)_4 \end{matrix}\!\!>\!CHBr + NH_3 = \begin{matrix} CH_3 \\ CH_3(CH_2)_4 \end{matrix}\!\!>\!CHNH_2.HBr.$$

1 I name those compounds which have the group or element characterizing them attached to the second carbon atom in the normal hydrocarbon chain, β-derivatives; thus $CH_3CH_2CH_2CH_2CH_2CHNH_2CH_3$ is called β-heptylamine.

2 Read at the Columbus meeting of the American Association for the Advancement of Science.

3 *Jsb. d. Chem.* (1863), 528.

4 *Ann. Chem.* (Liebig), **127**, 318.

5 *Ber. d. chem. Ges.*, **13**, 1650.

6 *Monatsh. Chem.*, **3**, 165.

7 *Ibid.*, **3**, 166 and 170.

The other is the splitting off of hydrogen bromide by the ammonia with the formation of heptylene and ammonium bromide as follows:

$$CH_3(CH_2)_4CHBrCH_3 + NH_3 = CH_3(CH_2)_4CH{=}CH_2 + NH_4Br.$$

Preparation of β-Heptylamine, $CH_3(CH_2)_4CHNH_2CH_3$.—β-Heptyl bromide, boiling-point 164°–168°, was sealed in a tube with an excess of an alcoholic solution of ammonia and heated in a water-bath for forty-eight to seventy-two hours; at the end of this time the reaction was apparently complete. The contents of the tube were filtered to remove ammonium bromide, which had formed in some quantity. The alcohol was then distilled off and the residue heated for some time in a partial vacuum at about 125° in order to free it from unchanged β-heptyl bromide or other impurities volatile at that temperature and pressure. The crude β-heptylamine hydrobromide, obtained in this manner, was dissolved in a small quantity of warm benzene and petroleum ether added until the clear liquid was slightly turbid.

After warming on a water-bath until clear and allowing to stand for some hours, fairly pure β-heptylamine hydrobromide crystallized out. The purified hydrobromide was dissolved in a small quantity of water and an excess of potassium hydroxide solution (1 : 1) added. Although there was evolution of heat and the separation of the amine seemed complete, the mixture was heated fifteen minutes on a water-bath to be sure that all the base had been liberated. The free β-heptylamine, floating on the potash solution, was separated and the solution extracted with ether. After drying the ethereal solution with solid potassium hydroxide and distilling off the ether, a slightly brown colored liquid was obtained, which was distilled in a partial vacuum from anhydrous barium oxide, over which it had stood for five days. When carefully fractioned at ordinary pressures, the greater portion distilled at 142°–144° (most at 143°). The density of this fraction at 24° compared with water at the same temperature is 0.7667.

On diluting the alcohol which was distilled from the crude hydrobromide, an oil separated. This was roughly divided by distillation into two fractions, the lower boiling being heptylene, as it had the characteristic odor, and absorbed bromine; the

higher boiling fraction was unchanged β-heptyl bromide as was shown by its boiling-point and the presence of bromine.

β-Heptylamine is a colorless liquid with a very characteristic amine-like odor and bitter, burning taste. It is soluble in alcohol, ether, or petroleum ether; slightly soluble in water. It takes up some water, from which it is freed with the greatest difficulty. It is strongly alkaline, combining with acids with evolution of much heat. If left in the air, it absorbs water and carbon dioxide.

I. 0.2317 gram of the amine gave 0.6166 gram carbon dioxide and 0.3140 gram water.

II. 0.1353 gram of the amine gave 15.5 cc. nitrogen at 28° and under a pressure of 752 mm.

III. 0.2844 gram of the amine gave 33 cc. nitrogen at 29° and under a pressure of 752 mm.

	Calculated for $C_7H_{17}N$.	Found. I.	II.	III.
Carbon	73.05	72.58		
Hydrogen	14.78	15.06		
Nitrogen	12.16		12.43	12.52

β-Heptylamine Hydrobromide, $CH_3(CH_2)_4CHNH_2CH_3.HBr$.—The fairly pure β-heptylamine hydrobromide as obtained in the preparation of β-heptylamine was recrystallized from a mixture of benzene and petroleum ether until the melting-point was constant.

β-Heptylamine hydrobromide crystallizes in exceedingly fine, white, silky needles, which are two to three cm. in length and melt at 163°. It is very soluble in alcohol, benzene, and water; soluble in a large volume of dry ether, practically insoluble in petroleum ether.

I. 0.3125 gram of the substance gave 0.2980 gram silver bromide.

II. 0.3988 gram of the substance gave 0. 3836 gram of silver bromide.

	Calculated for $C_7H_{18}NBr$.	Found. I.	II.
Bromine	40.81	40.57	40.93

β-Heptylamine Hydrochloride, $CH_3(CH_2)_4CHNH_2CH_3.HCl$.—This salt was prepared by passing hydrochloric acid gas into an ethereal solution of β-heptylamine. As the ether was not com-

pletely dry, it did not all precipitate as was expected, therefore the ether was allowed to evaporate. The slightly colored residue, obtained in this manner, was dissolved in warm benzene, petroleum ether added until slightly turbid, and set aside to crystallize. Crystallization was repeated until the melting-point was constant.

β-Heptylamine hydrochloride crystallizes in beautiful, white, silky, slightly deliquescent needles, which melt at 133°. It is readily soluble in water, alcohol, and benzene; insoluble in petroleum ether and sparingly soluble in ether.

I. 0.2198 gram of the substance gave 0.4460 gram carbon dioxide and 0.2322 gram water.

II. 0.1928 gram of the substance gave 15.4 cc. nitrogen at 19° and under a pressure of 753 mm.

III. 0.2029 gram of the substance gave 18 cc. nitrogen at 19° and under a pressure of 753 mm.

IV. 0.3345 gram of the substance gave 0.3140 gram silver chloride.

V. 0.3618 gram of the substance gave 0.3370 gram silver chloride.

	Calculated for $C_7H_{18}NCl$.	Found. I.	II.	III.	IV.	V.
Carbon	55.45	55.35				
Hydrogen	11.88	11.74				
Nitrogen	9.24		8.88	9.87		
Chlorine	23.43				23.21	23.09

β-Heptylamine Chlorplatinate, $(C_7H_{15}NH_2.HCl)_2PtCl_4$, was prepared from the amine hydrochloride by dissolving it in a small amount of water and adding an excess of chlorplatinic acid. The salt separates in fine plates which are sparingly soluble in cold, easily in warm water. It crystallizes from the latter on cooling, in large yellow plates. It is readily soluble in alcohol. On heating to 195° it decomposes.

0.2164 gram of the salt gave 0.0653 gram platinum.

	Calculated for $C_{14}H_{34}NCl_6Pt$.	Found.
Platinum	38.23	37.98

β-Heptylamine Chloraurate, $C_7H_{15}NH_2.HClAuCl_3$, was prepared by adding chlorauric acid to a concentrated solution of the

amine hydrochloride in water. It separates in light yellow crystals which melt at 63°–64°. In cold water it is sparingly soluble; readily soluble in warm water from which it may be crystallized in large yellow plates.

0.1805 gram of the salt gave 0.0778 gram gold.

	Calculated for $C_7H_{17}NCl_4Au$.	Found.
Gold	43.30	43.10

β-Heptylamine Oxalate, $(C_7H_{15}NH_2)_2C_2H_2O_4$, was prepared by adding the amine in slight excess to an alcoholic solution of oxalic acid, precipitating with ether, and recrystallizing from alcohol. It crystallizes in beautiful, white plates, which melt at 204°–205° with decomposition. In cold water or alcohol it is moderately soluble; in the warm solvents it is readily soluble. It is insoluble in ether and petroleum ether. On boiling it with water it is completely decomposed, the oxalic acid remaining and the β-heptylamine passing off with the steam.

I. 0.2545 gram of the substance gave 0.5626 gram carbon dioxide and 0.2605 gram water.

II. 0.1873 gram of the substance gave 0.4122 gram carbon dioxide and 0.1882 gram water.

III. 0.2900 gram of the substance gave 24.8 cc. nitrogen at 18° and under a pressure of 753 mm.

IV. 0.2658 gram substance gave 20.7 cc. nitrogen at 18° and under a pressure of 753 mm.

	Calculated for $C_{16}H_{36}O_4N_2$.	Found.			
		I.	II.	III.	IV.
Carbon	60.00	60.30	60.03		
Hydrogen	11.25	11.37	11.17		
Nitrogen	8.75			8.35	8.90

At the time I made the nitrogen determinations given in this paper, the apparatus was inadequate, which will, in part, account for the poor results obtained.

The study of β-heptylamine is being continued in this laboratory.

I wish to express my sincere thanks to Dr. F. P. Venable for his advice and interest in the prosecution of this task.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF NORTH CAROLINA, July 28, 1899.

THE AMOUNT OF HUMUS IN SOILS AND THE PERCENTAGE OF NITROGEN IN THE HUMUS, AS AFFECTED BY APPLICATIONS OF AIR-SLAKED LIME AND CERTAIN OTHER SUBSTANCES.

By H. J. Wheeler, C. L. Sargent, and B. L. Hartwell.

Received August 14, 1899.

IT is a well-known fact that lime, under favorable conditions, hastens the decomposition of organic matter. Notwithstanding this fact, however, lime is a most beneficial substance to apply to certain soils if used in rational quantities in connection with other manures, and provided such a system of manuring and cropping is employed that a sufficient supply of humus is maintained whether by the use of stable manure, muck, green manures, or by the occasional turning under of a grass sod.

In consideration of the interesting observations by Hilgard and Jaffa,[1] showing that the nitrogen content of the humus of certain soils of the arid regions of the United States exceeded in several instances eighteen per cent., and in view of the idea advanced later[2] by Hilgard to the effect that the nitrogen percentage of the humus may probably be taken as an indication of the degree of immediate assimilability of the nitrogen of soils, it seemed desirable to make a study of our own soil in its natural state and as affected by liming. The surface soil employed in this experiment came from plot OO of the cooperative acre located between fields B and C, and the subsoil was taken at the north end of the series of plots of which plot OO formed a part.[3] The surface soil and subsoil were each thoroughly mixed before being placed in the pots. The pots employed were galvanized iron ash-cans about twenty-six inches deep, and eighteen inches in diameter with bottoms inclined toward the center, at which point an opening was left to insure drainage. The pots were set into the soil to within two inches of the tops and agricultural drain tiles laid underneath, to prevent the ingress of surrounding soil-water. One hundred and fifty-four pounds of subsoil, and 100 pounds of surface soil were placed in each pot.

[1] *Agricultural Science*, 8, 165 (1894),

[2] Bulletin 47, U. S. Department of Agriculture, Division of Chemistry, pp. 58-60.

[3] See chart of experimental plots, Ninth Annual Report, Rhode Island Agricultural Experiment Station (1896).

The pots were filled in the spring of 1893. In 1893 and 1894 each manured pot received 7.36 grams of potassium chloride and 22.07 grams of dissolved bone-black. In the succeeding years, these amounts were increased to ten and twenty-five grams respectively. Wherever nitrogen was applied, it was at the rate of 2.65 grams per pot. Lime, unless otherwise specified, was applied in the form of air-slaked lime, practically free from magnesia, at the rate of 147.2 grams per pot (four tons per acre). Gypsum was applied so as to furnish the same amount of calcium oxide as the air-slaked lime at the rate of four tons per acre. Rhode Island capped corn (maize) was grown in the pots in 1893, oats in 1894, and spring rye in 1895. The soil employed in making the determinations was removed from the pots late in the autumn of 1895, or some weeks subsequent to the harvesting of the rye. In the case of pots which had been manured alike, approximately like amounts of soil were taken from each, and the samples for analysis were then taken from the mixture of these lots.

The following were the methods of analysis employed in the determination of humus and nitrogen in the humus: Humus was determined by first extracting the soil (twenty grams) with dilute hydrochloric acid as proposed by Hilgard,[1] but with the employment of an automatic washing apparatus, until no further reaction for lime was obtainable in the wash solution. The acid was then removed by successive washings with water until the wash-water was neutral.

In the subsequent treatment with ammonia, the Huston and McBride,[2] modification of the Grandeau method was employed. By this modification, the time of treatment and relation between volume of solvent and the quantity of material extracted, are constant factors. This seemed to be desirable in comparative tests, of the character under consideration. Successive extractions as proposed by Snyder[3] would undoubtedly have given even greater percentages of extract, since many extractions are necessary in the case of our upland soils to remove everything which can be dissolved by ammonia. It is not improbable, however, that a portion of the more insoluble extract may not be

[1] Wiley's Principles and Practice of Agricultural Analysis, Vol. I, p. 325.
[2] Wiley's Principles and Practice of Agricultural Analysis, Vol. I, pp. 327–328.
[3] Annual Report Minnesota Agricultural Experiment Station, 1893, pp. 251–252.

strictly humus, but may consist of unhumified matter extracted by the ammonia from plant residues.

The nitrogen in the humus was determined by using a two and one-half per cent. solution of potassium hydroxide in place of the solution of ammonium hydroxide of like strength, which was employed in the determination of humus. Aliquot portions of the extract were then neutralized with sulphuric acid, and after evaporating to dryness in a Kjeldahl flask, the nitrogen was determined as usual by the method of Kjeldahl. The soils were air-dried before analyzing, and the different samples contained from 2.00 to 2.75 per cent. of water, determined at 100° C. The following are the analytical results obtained, calculated to percentages of *dry* soil.

Nos. of pots.	Manures applied.[1]	Humous nitrogen in dry soil.	Humus in dry soil.	Nitrogen in dry humus.
21	Unmanured	0.130	3.86	3.37
16, 18, 25	Ammonium sulphate	0.128	3.93	3.26
15, 22	Ammonium sulphate, air-slaked lime (1 ton per acre)	0.133	3.77	3.53
17, 19, 26	Ammonium sulphate, air-slaked lime (4 tons per acre)	0.126	3.63	3.47
1, 8	Ammonium sulphate, calcium sulphate (land plaster) at a rate equivalent in CaO to 4 tons of air-slaked lime per acre	0.139	3.65	3.81
20, 27	Without nitrogen and lime	0.129	3.75	3.44
23, 24	Air-slaked lime (4 tons per acre)	0.139	3.51	3.68
6, 13	Sodium nitrate	0.143	3.93	3.64
7, 14	Sodium nitrate and air-slaked lime (4 tons per acre)	0.133	3.42	3.89

A study of the foregoing table reveals certain points of interest. Comparing the result from the pot which was unmanured (21), with that from those pots where potash and phosphoric acid were applied annually (20 and 27), it will be seen that the humus nitrogen and the percentage of humus had become but slightly less where the manures were applied, than in the unmanured soil, while the percentage of nitrogen in the dry humus showed also but slight variation.

[1] All of the pots except No. 21, received like amounts of potash and phosphoric acid.

By a comparison of the result where potash and phosphoric acid were employed (20 and 27), with that from the pots which received an additional application of lime (23 and 24), it appears that where lime was applied, the humus nitrogen in the soil had increased, and the percentage of humus had decreased 0.24 per cent., while the percentage of nitrogen in the humus had been augmented by 0.24 per cent.

In the case of the pots receiving nitrogen as sodium nitrate (6, 13, 7, and 14), it will be seen that the percentage of humus nitrogen was lower in the limed ones (7 and 14), and the humus was 0.51 of a per cent. lower but the percentage of nitrogen in the humus itself was 0.25 per cent. higher.

From an inspection of the results from the limed and unlimed ammonium sulphate pots (16, 18, 25, 15, 22, 17, 19, and 26), it will be seen that where lime was applied at the rate of one ton per acre (pots 15 and 22), the humus nitrogen was slightly greater, the humus was 0.16 per cent. less, and again the percentage of nitrogen in the humus itself was 0.27 per cent. greater.

In the case of the pots receiving lime at the rate of four tons per acre (pots 17, 19, and 26), no decided variation in the amount of humus nitrogen resulted, though the percentage of humus was found to be three-tenths per cent. less than where no lime was used, and, as in each of the other cases cited, the percentage of nitrogen in the humus was increased by liming.

Where calcium sulphate (gypsum or land plaster) was applied (pots 1 and 8), so as to furnish an amount of calcium oxide equivalent to that supplied by the air-slaked lime at the rate of four tons per acre, the humus nitrogen was 0.011 of a per cent. higher than where neither lime nor gypsum was applied (pots 16, 18, and 25), the humus was 0.28 of a per cent. lower, and the percentage of nitrogen in the humus 0.55 per cent. higher.

From the foregoing it will be seen that without exception the addition of air-slaked lime or gypsum resulted in lowering the total amount of humus, as compared with the unmanured plot, yet in every instance the percentage of nitrogen in the humus had been increased. In fact the latter statement applies also even where no nitrogen was added (pots 23 and 24).

Where lime was not applied, but nitrogen was employed in form of ammonium sulphate, which in the acid soil proved

poisonous to plants (pots 16, 18, and 25), it will be observed that the percentage of nitrogen in the humus was even less than where no manure was used (pot 21). On the contrary, where nitrogen in the form of sodium nitrate, was added without lime (pots 6 and 13), the percentage of nitrogen in the humus was greater than in the case of the unmanured soil (pot 21).

It is also of special interest to observe that in the case of the unlimed soil which received potash and phosphoric acid, but no nitrogen (pots 20 and 27), the percentage of humus became less than in the unmanured soil, while on the contrary, where nitrogen was applied as sodium nitrate, and as ammonium sulphate, to unlimed soil, it is possible that a slight increase in the percentage of humus resulted. The differences are not great enough, however, to furnish any positive evidence in this respect.

From what has preceded, in relation to the percentage of nitrogen in the humus, it seems probable, in case the view of Hilgard is correct, that the use of lime had actually increased the immediate assimilability of the humus nitrogen, notwithstanding the fact that the heaviest crops were produced by the limed pots. This is especially interesting in view of the fact that Hilgard and Jaffa[1] in twelve years' continuous cropping with grass upon soil of the California Station, found an increase of two-tenths per cent. in humus, but a decrease of nitrogen in the humus from eighteen to three per cent.

Lime has, as shown, decreased the percentage of humus, yet this has been in the case of continuous culture of cereals. In consideration, however, of the wonderful increase of roots and residual organic matter in our limed soils when they are seeded to grass, as compared with those which are unlimed, and since lime is well known to facilitate the humification of organic matter within the soil, there appears to be no danger of impoverishing the soil humus by the reasonable use of lime, wherever the land is occasionally left in grass for a few years, or where the supply of organic matter is maintained by the use of sufficient muck, stable manure, or by plowing in an occasional green crop. It is of considerable interest to note, where lime was applied, that notwithstanding the fact that the total humus was reduced, the percentage of nitrogen in the humus was increased in every case. However, this is in accord with the conditions which pre-

[1] Bulletin 47, U. S. Department of Agriculture, Division of Chemistry, 1895, p. 59.

vail generally where plant residues undergo decay. Hydrogen and oxygen are eliminated as water and carbon dioxide, more rapidly than nitrogen is eliminated.

Where sodium nitrate was applied without the use of lime, the percentage of humus nitrogen was greatest of all and the percentage of humus reached its maximum. The nitrogen in the humus was also two-tenths per cent. above that where nitrogen and lime were omitted (pots 20 and 27), and 0.27 per cent. above that where no manure was used (pot 21). This is particularly interesting in view of the fact that the unlimed sodium nitrate pots produced each season greater crops than pot 21, 20, or 27. These data indicate, therefore, a storage of some of the nitrate nitrogen within the soil in the form of organic matter,[1] which becomes quickly soluble in ammonium hydroxide, or, in other words, passes largely into a condition which permits of its classification with that organic complex which is termed humus.

In the light of recent investigations, it is probable that this may be accomplished by means of the denitrifying organisms which, while liberating some of the nitrogen in the gaseous state, may nevertheless store a portion in the soil in organic combinations. This view is also supported by the fact that lime decreases the activity of the denitrifying organisms, and that no such marked indications of the storage of nitrate nitrogen were observed where lime was employed. At all events, if these indications are verified by future investigations, it would seem probable that the disappearance of the nitrate nitrogen from a soil may not indicate the total loss of the nitrogen by cropping, drainage, and by elimination as gas, but that, under certain conditions, some portion of it at least may be transformed into a more stable form, which will subsequently become gradually available to plants.

It is to be regretted that opportunity has not been afforded to determine the total nitrogen content of the soils, together with the relative amounts of ammonium compounds, nitrates, and nitrites. It is hoped, however, that further time and means will become available in order that these interesting questions can be more extensively and thoroughly studied.

LABORATORY OF THE RHODE ISLAND
AGRICULTURAL EXPERIMENT STATION.

[1] Berthelot records a similar observation and concluded that it was due to purely chemical processes or to the activity of micro-organisms. *Compt. rend.*, 106, 638 (1888), abs. in *Chem. Centrbl.*, p. 486 (1888), cited from *Jsb. Agriculturchemie*, p. 22 (1888).

NOTE ON THE COLOR OF CHLORINE SOLUTIONS.

By E. H. Sarles.

Received August 7, 1899.

SOME time ago it was noticed that upon passing chlorine into ethyl alcohol to make chloral, the liquid finally separated into a lower yellow layer, and an upper green layer. The upper layer was a grass-green, not a yellowish green.

It seems therefore that chlorine can dissolve with a green color as well as with the usual yellow color. This fact has apparently been overlooked, for a considerable search through the chemical literature has revealed no record of a green-colored solution of chlorine; the matter seemed therefore worth looking into.

Litmus paper was immediately bleached by the green liquid but, upon blowing air through to remove uncombined chlorine, the bleaching power disappeared, the liquid losing its green color and giving simply an acid reaction. The color also disappeared upon passing carbon dioxide through the green liquid and upon standing for several hours exposed to the air. These facts would indicate a true solution of chlorine, chloral, chloroform, carbon disulphide, all giving yellow-colored solutions; no trace of green was observed by the naked eye.

After fractionating the green liquid and passing chlorine into the fractions, the green color reappeared only in the fractions boiling below 94° C., but the result was not satisfactory as the color of the fraction had lost much of the original green brilliancy. This indicates that the solvent is either easily decomposed or that it is very volatile, and that consequently only a small part is caught on distilling. This indication is strengthened by the fact that after several fractionations, the green color is lost entirely and cannot be regained on adding chlorine.

Considerable time has been spent in seeking the conditions most favorable to the formation of the green solution. The best results have so far been obtained by cooling the alcohol to about —15° C. with ice and crystallized calcium chloride while passing chlorine in. These results are preliminary; I intend to carry the investigation to some conclusion and hope to be able to announce the result soon.

Rutgers College,
August 5, 1899.

IMPROVEMENT IN THE CHEMICAL COMPOSITION OF THE CORN KERNEL.[1]

By Cyril G. Hopkins.

Received August 25, 1899.

THE many different uses which are made of corn and the enormous value of the crop to the United States may certainly be deemed sufficient reason for investigating the possibility of making improvements in the chemical composition of this important grain. The nature of any desired improvement will, of course, depend upon the use which is to be made of the crop produced. For example, if corn is grown for the manufacture of starch, glucose-sugar, sirup, or alcohol, it is desirable that the grain contain a high percentage of carbohydrates, and that the percentages of its other chief constituents, protein and fat, should be reduced as much as possible. If corn is used as feed for growing animals, or manufactured into corn flour for human food, a higher percentage of protein will certainly increase its value. If it is to be used chiefly for fattening stock, an increased percentage of fat might be the improvement to be desired. That the chemical composition of corn can be changed seems reasonably probable from the changes which have been produced in some other plants,—notably in the sugar-beet.

Before the work reported in this paper could be begun, it was found necessary to make a chemical study of the corn plant, and to devise methods for conducting experiments with the object of improving the composition of the grain. It is known that the mineral content of plants can be changed to some extent by the addition to the soil of mineral materials in a form readily available to the plant, but that the temporary change thus effected would have any appreciable hereditary tendency seems very unlikely. The method of procedure which seemed most promising is based upon the common method of making improvement in animals; namely, selecting the best examples of the desired type and breeding successively and under the best conditions from that stock, retaining from each generation only the highest types obtained. This is practically the method by which the

[1] Read before the American Chemical Society at the Columbus meeting held on August 21 and 22, 1899. This is an abstract from advance sheets of a bulletin on this subject, which will be published by the University of Illinois Agricultural Experiment Station as Bulletin No. 55, which will give the full data and details of these experiments.

sugar content of certain varieties of beets has been increased from less than five per cent. to twelve or even to sixteen per cent. A small portion of a beet is analyzed and, if it is found to be sufficiently rich in sugar, the beet is then set out, or planted, as a "mother," or seed, beet. From the seed produced beets are grown and another selection of seed beets is made on the basis of their sugar content. But the kernel of corn is not sufficient in quantity to make a complete chemical analysis by any practical method, and certainly the same kernel could not be used for analysis and also for seed.

Early in the year 1896 the writer began a special study of the chemistry of corn. Among the important facts indicated by the results obtained at that time were the following:

1. That the ear of corn is approximately uniform throughout in the composition of its kernels.

2. That there is a wide variation in the chemical composition of different ears of the same variety of corn.

That these conclusions are correct has been fully shown by some more recent work.[1] Approximate uniformity in the composition of the kernels, or grain, from the individual ear of corn has been established by the concordant evidence of a large number of analyses of parts of ears, and of many ash determinations and protein determinations in single kernels of corn. This may be illustrated by quoting the percentages of protein found in ten different kernels from each of two different ears:

High-protein ear.		Low-protein ear.	
Kernel No.	Protein.	Kernel No.	Protein.
1	12.46	1	7.45
2	12.54	2	7.54
3	12.44	3	7.69
4	12.50	4	7.47
5	12.30	5	7.74
6	12.49	6	8.70
7	12.50	7	8.46
8	12.14	8	8.69
9	12.14	9	8.86
10	12.71	10	8.10

The following *highest* and *lowest* percentages of the more important constituents of the corn kernel, found in analyzing fifty different ears of a single variety of corn, may serve to illus-

[1] For complete data see University of Illinois Agricultural Experiment Station, Bulletin 53, 150–157 (1898).

trate the wide variation in the composition of corn from different ears :

	Ash.	Protein.	Fat.	Carbohydrates.
Maximum.....	1.74	13.88	6.02	85.79
Minimum	1.09	8.35	3.95	78.92
Difference	0.65	5.53	2.07	6.87

With every constituent the variation is greater than Flechig[1] found with thirteen different varieties, and it is nearly as great as found by the Connecticut Experiment Station[2] with about seventy-five different varieties of corn grown under ninety presumably different conditions.

The uniformity of the individual ear of corn makes it possible to determine very approximately the composition of the grain by analyzing a sample consisting of a few rows of kernels from the ear. The remainder of the kernels of the ear may then be planted if desired. The wide variation in composition between different ears is a very important factor in the work of selecting seed, as a starting-point is thus furnished in each of the several lines of desired improvement.

The general plan[3] of the experiments to improve the chemical composition of corn was to make analyses of samples from a large number of ears, select for seed those ears which were found to contain a high percentage of the desired constituent, plant in an isolated field (to avoid cross fertilization from other corn), and grow the crop under as good field conditions as possible. From the crop obtained a large number of ears are selected, and samples of each ear are analyzed, seed being taken, as before, from those ears which are found to be highest in the percentage of the constituent which it is desired to increase. Each year this process is repeated. While it may require ten or twenty years' work to enable one to form a very definite opinion as to the extent to which it is possible to influence the chemical composition of corn, it is believed that the data and results thus far obtained may be of practical and scientific interest.

[1] Landwirtschaftliche Versuchs-Stationen, **32**, 17 (1886).

[2] Connecticut Agricultural Experiment Station, Annual Report (1893).

[3] All work reported in this paper was done upon a single variety of corn, commonly known as Burr's White. It has been grown for several years by the Illinois Agricultural Experiment Station with precautions to keep the variety pure and distinct. The analytical methods employed in the work herein reported have been described in detail in Bulletins 43 and 53 of the Illinois Station. All results are reported on the basis of dry matter, or water-free substance.

From the 1896 crop of Burr's White corn grown upon the Illinois Experiment Station farm, two bushels, or 163 ears, of good sound ear corn, suitable for seed, were selected. From each ear a sample consisting of three rows of kernels, lengthwise of the ear, was taken for analysis. From this lot of 163 ears, four different sets of seed corn were selected on the basis of chemical composition:

1. A set of twenty-four ears, each of which contained a high percentage of protein.

2. A set of twelve ears, whose percentage of protein was comparatively low.

3. A set of twenty-four ears, found to contain a high percentage of fat.

4. A set of twelve ears, containing a low percentage of fat.

Plans were made to carry on separately four direct experiments to change the chemical composition of corn; namely, (1) to increase the percentage of protein, (2) to decrease the protein, (3) to increase the fat, and (4) to decrease the fat. It is, of course, manifest that if the percentages of both protein and fat are increased, the percentage of carbohydrates must necessarily be decreased, and *vice versa*. By planting plots with both high-protein and low-protein corn, or with both high-fat and low-fat corn, results may be obtained which show the influence of selected seed, as independent and distinguishable from the effects due to the influence of the season.

In the spring of 1897 the four sets of corn which had been selected were planted on four different fields, or plots, each of which was fairly well isolated from other corn fields in order to avoid cross fertilization by corn of different chemical composition. For convenience these four plots are called: 1. High-protein plot; 2. Low-protein plot; 3. High-fat plot; 4. Low-fat plot. Invariably the seed planted in each row was all taken from a single ear; so that the high-protein plot, for example, contained twenty-four rows planted with seed from the twenty-four ears selected for that purpose. In the high-protein and high-fat plots the seed containing the very highest percentage of the desired constituent was planted in the middle rows, the remainder of the seed being planted in approximately uniform

gradation to either side. In the low-protein and low-fat plots the seed containing the very lowest percentages of protein and fat, respectively, was planted in the middle rows. This arrangement may be clearly seen by referring to the tables. The plots were given ordinary cultivation, and a good crop of corn was grown on each. When the corn was harvested a set of ten good ears was selected from each row, excepting from some outer rows. From some of the middle rows duplicate sets of ten ears each were taken from the same row, as will be seen from the tables, the analytical data from such rows being given in duplicate in all cases. Two rows of kernels (lengthwise of the ear) were taken from each of the ten ears and mixed to form a composite sample for analysis to represent the good corn grown on each row in the plots.

EXPERIMENTS TO INFLUENCE THE PROTEIN IN CONTENT OF CORN.

The results from the experiments to change the percentage of protein in corn will be first considered. The following tables are arranged to show the percentage of protein in the dry matter of the seed planted and the crop produced in 1897. For reference, the laboratory serial numbers of all samples whose analyses are herein shown are also given.

TABLE 1.—PROTEIN IN CORN PLANTED AND HARVESTED ON HIGH-PROTEIN PLOT IN 1897.

	Corn planted.		Corn harvested.	
Plot row No.	Corn No.	Protein. Per cent.		Protein. Per cent.
1	94	11.89	270	9.61
2	86	12.07	275	11.07
3	230	12.10	280	10.94
4	213	12.40	285	11.48
5	100	12.28	290	10.85
6	119	12.38	295	11.64
7	227	12.63	300	11.46
8	153	12.51	305	11.57
9	175	12.68	310	11.17
10	84	12.79	315	11.14
11	110	12.81	320	11.16
12	126	13.87	325	11.60
			330	11.31
13	92	12.96	335	11.07
			340	11.44

Plot row No.	Corn planted. Corn No.	Corn planted. Protein. Per cent.	Corn harvested. Corn No.	Corn harvested. Protein. Per cent.
14	177	13.06	345	10.89
			350	10.67
15	188	13.10	355	10.34
			360	11.48
16	232	12.76	365	11.05
17	87	12.40	370	10.75
18	204	12.57	375	10.86
19	105	12.36	380	11.07
20	141	12.42	385	10.88
21	172	12.28	390	11.73
22	222	12.34	395	10.76
23	147	12.21	400	11.30
24	208	12.05	405	11.53
	Plot averages,	12.54		11.10

TABLE 2.—PROTEIN IN CORN PLANTED AND HARVESTED ON LOW-PROTEIN PLOT IN 1897.

Plot row No.	Corn planted. Corn No.	Corn planted. Protein. Per cent.	Corn harvested. Corn No.	Corn harvested. Protein. Per cent.
1	151	9.31	....	....
2	114	9.12	410	10.55
3	83	9.08	415	10.89
4	225	9.15	420	10.26
5	116	8.38	425	10.10
6	145	8.25	430	10.73
			435	9.90
7	99	8.40	440	10.36
			445	10.20
8	215	9.22	450	9.89
9	185	9.33	455	10.24
10	164	9.36	460	11.20
11	113	9.30	465	12.24
12	193	9.47	....	....
	Plot averages,	9.03		10.55

The average composition of the corn from the high-protein plot shows a protein content of 11.10 per cent., while 10.55 is the average percentage of protein in the corn from the low-protein plot, indicating that the difference, 0.55 per cent., may be ascribed to the influence of the seed selection. On account of the plan, or order, in which the seed corn was arranged in the plots, that is, with the corn of highest protein content in the central rows of the high-protein plot, and the corn of lowest pro-

tein content in the central rows of the low-protein plot, we might expect to find a somewhat wider average difference in protein content if we consider only the corn grown on the central half of each plot. From rows 7 to 18 of the high-protein plot we find the average protein content of the corn produced to be 11.12 per cent., while 10.21 is the average percentage of protein in the corn from rows 4 to 9 of the low-protein plot, thus showing an average difference of 0.91 per cent.

From each set of ten ears from the 1897 crop, four of those which appeared most suitable for seed corn were reserved for further use. From each of these ears a sample consisting of three or four rows of kernels was taken for analysis. In order to retain hereditary influences the seed for the high-protein plot for 1898 was all selected from corn which grew from seed of high-protein content the previous year. On this account corn with high-protein content from the low-protein plot was rejected for seed. Likewise seed for 1898 for the low-protein plot was selected only from corn which grew upon that plot in 1897.

In conducting the experiments in 1898 the same general plan of the previous year was followed, and the results obtained were nearly the same as in 1897, and the data obtained from the high-protein and low-protein plots will not be given in this paper.

In order to avoid local differences in the soil conditions, a third plot of ground was planted in 1898 with corn of known protein content. For want of a better name this is called the "mixed-protein plot." It contained five rows of ten hills each. In each hill were planted four kernels of corn of which two were high and two were low in protein content. The kernels were so arranged in the hill that the stalk of corn produced from each could be known. When the crop was harvested eight to ten ears from both the high-protein seed and the low-protein seed were taken from each row. By taking two rows of kernels from each ear ten composite samples were made, of which five represent the corn grown from the high-protein seed, in the five rows, and the other five represent the corn produced in the same rows from the low-protein seed. The following table shows the protein content of the seed planted and of the samples taken from the crop harvested.

TABLE 3.—PROTEIN IN CORN PLANTED AND HARVESTED ON MIXED-PROTEIN PLOT IN 1898.

Plot row No.	Corn planted. Corn No.	Protein. Per cent.	Corn harvested. Corn No.	Protein. Per cent.	Corn planted. Corn No.	Protein. Per cent.	Corn harvested. Corn No.	Protein. Per cent.
1	408	12.80	698	11.24	446	8.84	697	9.72
2	326	13.62	700	11.75	458	8.22	699	11.04
3	407	12.72	702	12.10	427	8.29	701	10.09
4	304	11.97	704	11.65	416	8.88	703	10.89
5	364	11.89	706	11.81	448	9.05	705	10.58
		Plot averages,		11.71				10.46

The results of analysis show that in every row the high-protein seed produced corn with a higher protein content than that produced by the low-protein seed. The average protein content of the corn from the high protein seed is 11.71 per cent., while 10.46 is the average percentage of protein in the corn from the low-protein seed. This makes an average difference of 1.25 per cent. of protein which is attributable without question solely to the selection of seed on the chemical basis.

Incidentally it may be stated that the writer has found different ears of good sound Burr's White corn varying from 7.50 per cent. to 16.11 per cent. of protein in the dry matter. The fact that one good ear of corn with a protein content above 16 per cent. has been produced is a promise of the possibility of improving corn in that direction. Indeed, it is but reasonable to suppose that this limit may be reached again or even exceeded, and very possibly with corn in larger amounts than single ears.

Combined chemical and mechanical studies of the corn kernel have been reported by Salisbury,[1] Haberlandt and Lenz,[2] Atwater,[3], Voorhees,[4] and Balland.[5] The results obtained[6] show that the protein in the corn kernel is contained principally in the glutinous layer surrounding the main body of the kernel. This layer is very thin at the crown of the kernel but quite thick at the sides. The germ in the center of the tip end of the kernel is also rich in protein, although the entire germ constitutes

[1] Trans. N. Y. State Agricultural Society, **8**, 678 (1848).

[2] *Allgemeine land- und forstwirtschaftliche Zeitung*, 257 (1866); Hoffmann; *Jsb. Agricultur-Chemie*, 9, 106 (1866).

[3] Thesis, Yale College (1869); *American Journal of Science and Arts* [2], **48**, 352 (1869).

[4] New Jersey Agricultural Experiment Station, Bulletin 105 (1894).

[5] *Compt. rend.*, **122**, 1004 (1896).

[6] University of Illinois Agricultural Experiment Station, Bulletin 53, 138–140 (1898).

Fig. 1.

only about twelve per cent. of the kernel. The starchy portion, lying between the germ and the glutinous layer, consists almost entirely of carbohydrates, although the glutinous layer contains also a large percentage of carbohydrates.

On the basis of this knowledge of the general structure of the corn kernel and chemical composition of its several parts, the writer has made some investigations as to the possibility of selecting corn of high-protein content and of low-protein content by purely mechanical means, and has found that such a method is both possible and practicable. By making cross sections and longitudinal sections of several kernels from an ear of corn, one can judge with a very satisfactory degree of accuracy whether the corn is rich or poor in protein.

The illustration (Fig. 1) here shown was made from a photograph taken of the corn kernels and sections with a magnification of three diameters. At the left are two sections and a whole kernel from an ear of corn which contained 14.92 per cent. of protein. The sections and whole kernel at the right are from an ear containing 7.76 per cent. of protein. About one-fourth of the kernel was cut off from the tip end in making the cross sections. In the longitudinal sections the tip end of the kernel points upward to the right. It will be seen that in the cross sections the white, starchy layer nearly disappears in the high-protein corn but becomes very prominent in the low-protein corn. In the longitudinal sections this difference is also apparent, the white starch in the high-protein corn being confined almost entirely to the crown end of the kernel, while in the low-protein corn it extends into the tip in considerable amount. The germ in the high-protein corn is somewhat larger. This is also indicated by the size of the depressions in the whole kernels.

As an experiment about 300 ears of corn were examined by this mechanical method. Eighteen ears in the lot were picked out as possessing the physical characteristics which indicate a comparatively high content of protein, fifteen other ears which appeared to be low in protein being selected at the same time. Table 4 shows the results in detail, the percentage of protein in the corn from each ear being given as previously determined by chemical analysis.

TABLE 4.—ACTUAL PROTEIN CONTENT OF CORN SELECTED BY MECHANICAL EXAMINATION.

Ear No.	Corn selected for High protein. Per cent.	Low protein. Per cent.
1	11.47	11.48
2	12.04	9.06
3	9.69	9.90
4	11.78	9.15
5	11.65	9.67
6	11.38	10.11
7	11.64	9.11
8	11.22	10.25
9	11.97	8.63
10	11.94	9.63
11	10.96	8.61
12	10.83	10.95
13	11.87	11.27
14	10.21	9.36
15	11.71	10.25
16	11.59	....
17	12.31	....
18	10.54	....
Averages,	11.38	9.83

The average protein content of the eighteen ears selected for high-protein corn is 11.38 per cent., while 9.83 is the average percentage of protein in the fifteen ears selected for low-protein corn. The examination consists in simply cutting cross sections and longitudinal sections from the kernels with a pocket-knife and judging as to the combined amount of glutinous layer and germ in relation to the quantity of white starchy matter, the observation being made with the naked eye. In making the selections the time given to each ear was about half a minute, and it is not assumed that the writer possesses any special skill in the art of judging the comparative sizes of small areas, or surfaces, the chief point involved in making these examinations. It seems but fair to suppose that the average corn-grower could, with some practice and care, make a better selection than is here shown. The selections shown in Table 4 were made from material[1] which was at hand and for the purpose of showing the

[1] NOTE.—The percentage of protein in the different ears in this plot of corn did not vary as much as would ordinarily be the case, because thirty-four of the ears highest in protein, and twenty-six of those lowest in protein, had previously been removed from this stock of corn, having been selected by chemical analysis.

feasibility of the method, rather than the extent to which it may be carried.

EXPERIMENTS TO INFLUENCE THE FAT CONTENT OF CORN.

From the lot of 163 ears of corn from the 1896 crop, to which reference has already been made, seed was selected for the high-fat and low-fat plots for 1897. Good crops of corn were grown, and when harvested composite samples of corn from the different rows were taken and analyzed. The results obtained[1] indicate that the fat content of corn is influenced very markedly by selecting seed according to its percentage of fat. The difference between the average percentages of fat in the corn from the two plots is 0.67 per cent., the average from the high-fat plot being 4.73 and that from the low-fat plot 4.06 per cent. of fat. There is a difference of 0.79 per cent. of fat between the averages of the two crops if we consider only the central half of each plot. It is noteworthy that the lowest percentage of fat in the corn from any row of the high-fat plot is higher than the highest percentage obtained from any row in the low-fat plot.

From each set of ten ears from the 1897 crop four ears were taken for individual analysis, a sample of three or four rows of kernels (lengthwise of the ear) being taken from each ear for this purpose. For 1898 the seed for the high-fat plot was all from corn which grew from high-fat corn in 1897, twenty-four ears being selected. For the low-fat seed twelve ears were taken from the corn which grew from low-fat seed in 1897. The system of planting the highest of the high-fat seed and the lowest of the low-fat seed in the central rows of the respective plots was followed in 1898. Good crops of corn were grown, and when harvested sets of ten ears each were taken from each row, composite samples to represent each row being made, as before, by taking two rows of kernels from each of the ten ears. Tables 5 and 6 give the percentage of fat in the seed planted and in the crop produced, for each row of corn.

[1] The complete data are not given in this paper.

TABLE 5.—FAT IN CORN PLANTED AND HARVESTED ON HIGH-FAT PLOT IN 1898.

Plot row No.	Corn planted. Corn No.	Fat. Per cent.	Corn harvested. Corn No.	Fat. Per cent.
1	521	4.98	1240	4.86
2	533	4.98	1250	4.74
3	486	5.03	1260	4.94
4	531	5.04	1270	5.17
5	568	5.05	1280	5.36
6	528	5.12	1290	4.79
7	546	5.20	1300	4.87
8	534	5.27	1310	5.20
9	478	5.39	1320	5.16
10	511	5.44	1330	5.25
11	501	5.45	1240	5.21
12	524	5.68	1350	5.63
13	513	5.49	1360	5.21
14	512	5.45	1370	5.44
15	527	5.43	1380	5.48
16	514	5.39	1390	5.26
17	517	5.26	1400	5.55
18	559	5.12	1410	5.23
19	484	5.07	1420	5.06
20	544	5.02	1430	4.89
21	508	5.04	1440	5.00
22	547	5.00	1450	5.10
23	536	4.97	1460	5.05
24	494	4.97	1470	5.21
	Plot averages,	5.20		5.15

TABLE 6.—FAT IN CORN PLANTED AND HARVESTED ON LOW-FAT PLOT IN 1898.

Plot row No.	Corn planted. Corn No.	Fat. Per cent.	Corn harvested. Corn No.	Fat. Per cent.
1	589	3.85	1480	3.97
2	574	3.83	1490	4.32
3	592	3.72	1500	4.08
4	602	3.55	1510	3.99
5	594	3.39	1520	3.81
6	614	3.39	1530	3.81
7	593	3.38	1540	3.69
8	606	3.50	1550	3.78
9	588	3.70	1560	3.93
10	603	3.80	1570	4.18
11	611	3.84	1580	4.21
12	591	3.85	1590	4.11
	Plot averages,	3.65		3.99

The average fat content of the corn from the high-fat plot for 1898 is 5.15 per cent., while 3.99 is the average percentage of fat in the corn from the low-fat plot, making a difference of 1.16 per cent. between the averages. The difference becomes 1.45 per cent. if we consider only the central half of each plot, or 1.56 per cent. if only the central third of each plot is considered. Even the effect of planting the seed in gradation as to fat content from the center rows to either side is decidedly noticeable in the crop. It is only necessary to take averages of the fat content of the composite samples from the high-fat plot in groups of four to obtain a regular gradation in the same order as that of the seed. Thus:

Corn. From rows.	Fat. Average per cent.
1–4	4.93
5–8	5.06
9–12	5.31
13–16	5.35
17–20	5.18
21–24	5.09

In the low-fat plot the percentages of fat in the composite samples *from the single rows* are in regular gradation, if we omit only the outside rows, Nos. 1 and 12. This may be seen in Table 6.

In 1898 a third plot of ground for the study of the fat content of corn was planted. This is called the "mixed-fat plot," and was planted after the same plan as the mixed-protein plot. In each hill two kernels of high-fat corn were planted on one side and two of low-fat content on the other. The special object in this work was, of course, to avoid the influence of soil differences. From this mixed-fat plot twenty-seven pairs of ears were taken from twenty-seven hills, one ear in each pair having been grown from high-fat seed and the other ear from low-fat seed. Table 7 gives the fat content in the corn from each of these ears.

TABLE 7.— FAT IN CORN FROM FIFTY-FOUR EARS GROWN ON THE MIXED-FAT PLOT IN 1898.

Hill No.	From high-fat seed. Corn No.	Fat. Per cent.	From low-fat seed. Corn No.	Fat. Per cent.
1	762	4.05	761	3.82
2	764	4.42	763	3.62
3	766	4.65	765	3.03
4	768	4.90	767	3.92
5	770	5.16	769	3.94
6	772	5.06	771	3.99
7	774	5.13	773	4.15
8	776	4.95	775	3.75
9	778	5.59	777	3.60
10	780	4.10	779	4.04
11	782	4.49	781	3.56
12	784	5.25	783	4.26
13	786	5.65	785	4.15
14	788	5.03	787	4.08
15	790	5.57	789	3.57
16	792	5.32	791	4.69
17	794	5.75	793	3.96
18	796	4.95	795	4.64
19	798	4.79	797	4.30
20	800	4.59	799	4.33
21	802	5.56	801	3.77
22	804	5.34	803	4.17
23	806	4.92	805	4.50
24	808	5.91	807	3.58
25	810	5.86	809	4.55
26	812	4.59	811	3.96
27	814	5.02	813	4.23
	Averages,	5.06		4.01

The average percentage of fat in the twenty-seven ears from the high-fat seed is 5.06, while 4.01 per cent. is the average fat content of the twenty-seven ears from the low-fat seed. It is interesting to note that in the twenty-seven hills there is no instance where the ear of corn from high-fat seed does not contain more fat than the ear grown from low-fat seed in the same hill.

The ear which grew from low-fat seed in hill No. 3 has the lowest fat content, 3.03 per cent., of any ear of corn which has been analyzed in these experiments. The maximum fat con-

Fig. 2.

tent which has been found in an ear of Burr's White corn up to the present time is 6.71 per cent.

The fact that the fat, or oil, of the corn kernel is contained almost entirely in the germ[1] suggested to the writer the possibility of selecting corn of either high- or low-fat content by mechanical examination of the kernel and judging as to the quantity of germ compared with the remainder of the kernel. It was found that the method is possible and rather more satisfactory than the method (already described) of judging the protein content of the corn kernel by mechanical examination, as it is less complicated than the latter.

Figure 2 (made from a photograph taken with a magnification of three diameters) illustrates the difference in corn kernels of about the same size but a very different fat content. The cross sections shown at the top were made by cutting off about one-fifth of the kernel from the tip end. In the longitudinal sections the tip end of the kernel points downward to the left. The sections and whole kernel shown at the left are from an ear of corn which contains 6.08 per cent. of fat. Those at the right are from an ear containing 3.64 per cent. of fat. It will be seen that the germ is larger in the high-fat corn and that it extends nearly the entire length of the kernel, while in the low-fat corn the germ is small and only about two-thirds as long as the kernel.

To obtain exact data as to the relation between the percentage of fat and the percentage of germ in the corn kernel, the germs were removed[2] from a large number of kernels, the weight of the whole kernel and also of the separated germ being determined, and reported on the basis of dry matter, having been dried in hydrogen before being weighed. Table 8 will serve to illustrate the results obtained in this work.

[1] See University of Illinois Agricultural Experiment Station, Bulletin 53, 139, 140 (1898).

[2] It was found that after soaking corn kernels in hot water for about thirty minutes the germs are easily removed in the entire state and quite free from other portions of the kernel.

TABLE 8.—WEIGHT OF CORN KERNELS WITH WEIGHT AND PERCENTAGE OF GERMS.

Corn No. 1352—Fat = 6.71 per cent.				Corn No. 1529—Fat = 3.22 per cent.			
Kernel No.	Kernel weight. Gram.	Germ weight. Gram.	Germ. Per cent.	Kernel No.	Kernel weight. Gram.	Germ weight. Gram.	Germ. Per cent.
1	0.3113	0.0391	12.56	1	0.2859	0.0250	8.74
2	0.2872	0.0360	12.53	2	0.2882	0 0237	8.22
3	0.2864	0.0340	11.87	3	0.3533	0.0297	8.41
4	0.2821	0.0374	13.26	4	0.3135	0.0265	8.45
5	0.2667	0.0360	13.50	5	0.3277	0.0273	8.33
6	0.3694	0.0442	11.97	6	0.3417	0.0310	9.07
7	0.3434	0.0414	12.06	7	0.2918	0.0257	8.81
8	0.2682	0.0300	11.18	8	0.3178	0.0276	8.68
9	0.3116	0.0402	12.90	9	0.3273	0.0278	8.49
10	0.2870	0.0348	12.13	10	0.3338	0.0280	8.39
Av'ges,	0.3013	0.0373	12.40	Averages,	0.3181	0.0272	8.56

In corn No. 1352, containing 6.71 per cent. of fat, and corn No. 1529, containing 3.22 per cent. of fat, the kernels are approximately uniform in size, the former being 0.3013 and the latter 0.3181 gram in average weight; but the germs in the high-fat ear amount to 12.40 per cent. of the whole kernels, and to only 8.56 per cent. in the low-fat ear. This difference in percentage is due to the absolute difference in the size of the germs, the germs from the high-fat kernels being 0.0373 gram and from the low-fat kernels only 0.0272 gram average weight.

From a large amount of data the general relation between the percentage of fat and the percentage of germ in the corn kernel has been clearly established. Of course there are minor individual differences among the kernels from the same ear, and it has also been noted that there is a difference in different ears as to the relation between fat content and germ content. These minor differences are perhaps due in part to the varying percentage of fat in the body of the kernel, but the variation in the percentage of fat in the germs, especially from different ears, is doubtless the chief factor in producing such differences. For example, Voorhees[1] found 26.65 per cent. of fat in the germs of the corn kernel, while Balland[2] found 39.85 per cent.

The method of selecting corn of high- or low-fat content by mechanical examination is similar to that described under the work on the protein content of corn, excepting that the size of

[1] New Jersey Agricultural Experiment Station, Bulletin 105 (1894).
[2] *Compt. rend.*, **122**, 1004 (1896).

the germ alone as compared with the remainder of the kernel is considered. Judgment is formed by examining with the naked eye the cross sections and longitudinal sections of a few kernels from each ear. To make a practical test of the method nearly 300 ears of corn were examined, which varied in fat content[1] from about 3.60 to 5.80 per cent. From this lot of corn, by mechanical examination, eighteen ears were selected which appeared to possess a comparatively high-fat content, and at the same time thirty ears apparently low in fat were picked out. Tables 9 and 10 show the results in detail, the percentage of fat in the corn from each ear being given as previously determined by chemical analysis.

TABLE 9.—FAT CONTENT OF EIGHTEEN EARS SELECTED BY MECHANICAL EXAMINATION FOR HIGH-FAT CORN.

Ear No.	Fat. Per cent.	Ear No.	Fat. Per cent.
1	4.94	10	5.33
2	4.30	11	5.55
3	5.43	12	4.99
4	5.64	13	5.27
5	5.23	14	5.12
6	5.58	15	5.73
7	5.06	16	5.43
8	5.26	17	4.97
9	5.22	18	5.21
		Average,	5.24

TABLE 10.—FAT CONTENT OF THIRTY EARS SELECTED BY MECHANICAL EXAMINATION FOR LOW-FAT CORN.

Ear No.	Fat. Per cent.	Ear No.	Fat. Per cent.
1	4.01	16	3.63
2	4.11	17	4.02
3	3.64	18	4.55
4	3.67	19	4.52
5	4.52	20	4.29
6	3.66	21	3.81
7	4.07	22	4.39
8	4.20	23	4.43
9	3.91	24	3.80
10	4.85	25	4.09
11	4.35	26	4.27
12	4.52	27	4.02
13	3.73	28	3.87
14	3.76	29	4.00
15	5.21	30	3.98
		Average,	4.13

[1] Twelve ears of corn of very high fat content and sixteen ears of very low fat content had been previously taken from this lot and used for seed in 1899, otherwise the results would no doubt have been even more marked than they are.

The average fat content of the ears selected for high-fat corn is 5.24 per cent., while 4.13 is the average of that selected for low-fat corn. If we omit a single ear from each set, the lowest percentage of fat in the ears selected for high-fat content is higher than the highest percentage of fat in the low-fat selection.

SUMMARY AND DEDUCTIONS.

All results thus far obtained from our experiments indicate that it is not only possible but entirely practicable to influence the chemical composition of corn, that by proper selection of seed any of its principal constituents, protein, fat, or carbohydrates, may be increased or decreased.

In every experiment the selection of seed corn of high- and of low-protein content has produced marked effects in the crop, differences varying from 0.50 to 1.25 per cent. of protein; and in the experiments to influence the fat content of corn, the selection of seed of high- and of low-fat content has produced differences in the crops varying from 0.67 to 1.45 per cent. of fat.

Considering the fact that the average fat content of Burr's White corn is less than five per cent., the proportion of fat in corn is much more susceptible to the influence of seed selection than is the protein content. This is doubtless due to the fact that the primary materials from which fat is manufactured, namely, carbon dioxide and water, are usually furnished to the plant in unlimited supply, while the formation of protein is essentially dependent upon the supply of available nitrogen in the soil.

As the percentage of carbohydrates (principally starch in corn) varies inversely with the combined percentages of protein and fat (neglecting the small percentage of ash found in corn), it follows that the carbohydrates are increased in percentage whenever the combined percentage of protein and fat is decreased, and *vice versa*.

By actual trial it has been found both possible and practicable to select corn by mechanical examination with either high or low content of protein, fat, or starch.

While further investigations are necessary and are in progress to determine more accurately the best methods and more definitely the possibilities of improvement in the chemical composition of corn, it is here stated, tentatively, that essentially by the

methods reported in this paper any corn-grower will be able to select seed and to breed corn to increase or to decrease the percentage of any of its three principal chemical constituents.

All experiments reported in this paper have been carried on with the one variety of corn, namely, Burr's White. Of course it is not believed that Burr's White is the very best variety for improvement in corn in every one of the several important lines. Indeed, it seems highly probable that one variety of corn will be found best adapted to but one line of improvement. We have in progress chemical studies of other varieties of corn, and a considerable amount of data and information has been already acquired, but it is reserved, pending further investigations for future publication, the special object of this article being to give some of the data, thus far obtained, indicating the possibility and establishing the fact that the corn kernel may be improved in chemical composition.

It may be stated that improvement in the composition of other parts of the corn plant is under consideration by the Illinois Station. Plans are also made to investigate other questions relating to this general subject; such as the effect of changes in the chemical composition of corn upon its digestibility, vitality, yield, etc.

The results obtained in our investigations to improve the composition of corn have suggested the possibility of improving other grains by somewhat similar methods. It seems not improbable that the different grains, or kernels, produced in a single head of wheat, oats, or barley, may be found to be approximately uniform in composition.[1] If so, a method is thus afforded for selecting seed and breeding those cereals upon the basis of the chemical composition of the grain.

UNIVERSITY OF ILLINOIS
AGRICULTURAL EXPERIMENT STATION.

NOTE.

The Determination of Chromium in Steel.—A method for the determination of chromium in steel, based upon its oxidation to chromic acid by potassium chlorate in nitric acid, and the titration of the chromic acid with ferrous sulphate and potassium

[1] Since this was written a chemical study of wheat has been begun in this laboratory, and in general the results thus far obtained support the suggestion which is offered above.

permanganate in the greatly diluted solution, has been described by McKenna.[1] I have found it accurate and rapid. Sargent and Faust[2] suggest sand held in place by a little glass-wool, and covered by a very thin layer of asbestos, for filtering the nitric acid solution, in order to remove the oxides of manganese. I have found paper a suitable filtering medium for the removal of these oxides. Another change in details which I am accustomed to employ, is the use of nitric acid and potassium chlorate in greatly reduced quantities.

Dissolve three grams of the sample in fifty cc. of concentrated hydrochloric acid, in a 400 cc. lipped beaker, covering with a (five inch) watch-glass. Boil down until little more than a moist cake is left. Add fifty cc. of concentrated nitric acid, and boil for a few minutes when the copious evolution of nitrous fumes will have largely ceased. Remove from the light, and when somewhat cooled, add four grams of potassium chlorate, and resume the boiling, continuing until the solution is reduced in volume to from twenty-five to thirty cc. Dilute to 300 cc. with cold water, and add fifteen cc. of ammonia of 0.90 sp. gr. Mix thoroughly by stirring and filter the solution (first cooled if necessary) through a ribbed double paper, washing with cold water. Dilute the filtrate and washings to about 450 cc., and titrate with standard solutions of ferrous ammonium sulphate, and potassium permanganate. The best, that is the most accurate and simplest, way of standardizing these solutions is by means of a standard solution of potassium bichromate.

I have made some hundreds of experiments upon the amounts of reagents needed for the successful execution of this estimation, the extent to which the concentration by boiling must be carried, and the amount allowable of free nitric acid in the solution, before filtration through paper.

When three grams of steel are used for an estimation, from one to two grams of potassium chlorate are taken in many cases, and sometimes one-half gram, is sufficient to oxidize the chromium, if perfect removal of hydrochloric acid by nitric was first effected. The last traces of hydrochloric acid are, however, more conveniently removed by potassium chlorate.

It is evident that a solution of chromic acid if brought into

[1] Proceedings of Engineers' Society of Western Pennsylvania, 11, No. 6.
[2] This Journal, 21, 287.

contact with a paper filter, should be dilute and cold to avoid reduction. It is necessary also that not too much free nitric acid be present. The conditions for avoiding reduction by paper, are shown by the following results: They were obtained by titration of twenty cc. of potassium bichromate solution, which contained a quantity of chromium equal to 1.03 per cent. in three grams of steel. Each test was conducted as follows: the bichromate, nitric acid, and water were brought to the temperature desired, this being either nearly boiling, or cold to the touch, two washed papers placed in the beaker, and the whole stirred for five minutes, filtered through a ribbed paper, and the filtrate titrated after dilution to 450 cc.

Number of the experiment.	Nitric acid (1.42 sp. gr.) added before filtration. cc.	Temperature.	Volume filtered. cc.	Chromium expressed as a percentage for three grams of steel.	Remarks.
1....	0	..	..	1.03	No paper placed in this; no filtration.
2....	20	..	..	1.03	" " " " " " "
[1]3....	5	cold	300	1.03	
[1]4....	5	"	300	3.08	Sixty cc. of bichromate solution used.
5....	5	"	100	1.02	
6....	5	hot	100	0.95	
7....	10	cold	300	1.00	
8....	20	"	300	0.97	
9....	20	"	300	1.00	No paper placed in this; simply filtered.
10....	20	hot	300	0.96	" " " " " " "
11....	20	"	100	0.86	" " " " " " "

FOUR DETERMINATIONS OF CHROMIUM IN A CHROME STEEL.

Percentage of chromium.	
0.80	Filtered through asbestos.
0.81	" " "
0.81 } 0.81 }	Method described; filtering through paper.

RESULTS FROM ANALYZING SOLUTIONS OF KNOWN CONTENTS IN CHROMIUM.

These solutions were prepared as follows: three grams of steel containing no chromium were dissolved in hydrochloric acid, and a measured quantity of a standard solution of potas-

[1] Accuracy.

sium bichromate, reduced to chromic chloride by hydrochloric acid and alcohol, added.

These solutions were boiled down until little more than a moist cake was left, and the analysis in each case, further conducted exactly as described in the modified method, above given.

PERCENTAGE OF CHROMIUM.

True.	Found.
1.55	1.54
1.55	1.52
1.03	1.04
1.03	1.04
3.09	3.11

Addendum—Gravimetric Determination of Manganese in Steel.—The manganese precipitate collected upon a paper filter is a convenient starting-point for its gravimetric estimation. The solution of the precipitate in hydrochloric acid is to be treated in the customary way, the trace of iron being precipitated as basic acetate, and the manganese as manganous ammonium phosphate in the filtrate therefrom. R. W. MAHON.

NEW BOOKS.

THE DISCHARGE OF ELECTRICITY THROUGH GASES. By J. J. THOMSON, Professor in the University of Cambridge. New York: Charles Scribner's Sons. 1898. 203 pp.

This work of Prof. Thomson's represents the material of lectures delivered by him in October, 1896, at the sesquicentennial celebration of Princeton University, but amplified with a record of later observations. As the subject is one of comparatively recent date, it is hardly to be expected that the ground should have been so uniformly covered as to enable the writer to give a thoroughly connected account of the peculiar phenomena, that he and others have observed, in the fashion of a text-book. On the other hand, the fact that the essays were to be delivered orally precluded a purely historical presentation of discoveries, with a detailed account of the author's own work upon the subject. In place of these, we have a very lucid and fair exposition of the most striking facts, and an impartial statement of the most noteworthy hypotheses involved. The book is therefore chiefly useful as a guide through the intricate meshwork of hypotheses, which recent years have produced.

The difficulties of the subject seem to result largely from the impediments which interfere with the immediate observation of electrical phenomena in gases. In almost every case, the aid of solids or liquids must be called in, to convey the phenomenon to the observer, and the question often arises as to whether such phenomenon is not produced upon the surface of such liquid or solid.

The first chapter is devoted to the methods that can be employed for conveying an electric charge to a gas,—no easy task, according to the authors: liberation of the gas from a liquid undergoing electrolysis, the splashing of liquids through the gas, and the Röntgen rays, are resorted to. The second chapter, entitled photoelectric effects, really embodies the little that is known about the electric conductivity of gases, and its variation under the influence of different forms of radiant energy. Thomson apparently ascribes gaseous conduction to electrolysis, either in the purely chemical sense of the decomposition into ions, or in that of the association or dissociation of molecular complexes. A rather short chapter on the cathode rays has apparently been added as an extension of this hypothesis to the explanation of the results obtained by Lenard, Röntgen, and so many others. Contrary to the views of most of these physicists, Thomson ascribes the phenomena outside the vacuum tube to motions of gaseous matter, rather than of the "ether." As carriers of the rays, he looks for small particles, traveling at a high rate of speed and encountering fewer obstacles than would molecules or atoms. He assumes that atoms in fact consist of particles bearing the same relation to the total atom that the molecule does to the ordinary gas volume. Lockyer imagined that such particles were torn asunder by the heat of the solar atmosphere. Thomson thinks it likely that some higher order of electrolysis shatters the atoms that impinge upon the highly electrified cathode.

This, and other suggestive matter, is set forth in clear language and attractive style. The book is well printed and finely illustrated. MORRIS LOEB.

EASY EXPERIMENTS OF ORGANIC CHEMISTRY. By JOHN HOWARD APPLETON. Providence, R. I.: Snow and Farnham. 1898. 107 pp. Price, 60 cents.

There seems to be a general agreement in the study of

chemistry that, while the text-book work should be explained and illustrated by lectures, it should also be supplemented by laboratory work on the part of the student. Several excellent text-books on organic chemistry are now to be found in which a considerable number of illustrative experiments are described, but they are arranged to be performed either by the lecturer or by the student or by both, and in the attempt to satisfy two conditions they fail to meet either to the best advantage.

The book under consideration is intended solely for the student and for use in the laboratory, and it is characterized by a marked simplicity, directness and clearness of style, and by the very simple character of the apparatus and the very moderate amounts of materials to be employed, conditions which enable the untrained observer the more readily to observe the phenomena that occur, and to distinguish the essential from the non-essential.

No doubt, with such a fund of experiments to draw upon, as is now at the command of chemists, each person who sets out to arrange a course of experiments would prepare one that differed in some particulars from this, but Professor Appleton has selected fairly typical and instructive examples which can be performed in an easy and rapid manner, and he has arranged them in the order in which the topics are usually treated in text-books on organic chemistry so that the book can be used in connection with any introductory course, and it will be found to be a safe one to put into the hands of a student. A very commendable feature of the book is the "cautions" that are appended to the description of each experiment which is attended with any danger in its performance, for the author has thus relieved the teacher, in these instances, of a very grave duty.

CHARLES E. MUNROE.

A SELECT BIBLIOGRAPHY OF CHEMISTRY, 1492–1897. By H. CARRINGTON BOLTON. First Supplement. City of Washington: Published by the Smithsonian Institution. 1899. Large 8vo. ix + 489 pp..

This first supplement contains 5,554 titles in addition to the 12,031 contained in the volume issued in 1893. Of these, 2,050 titles were contributed by others. Many of the titles have, of course, been added by the author in bringing the book down to the close of 1897, but a considerable number have probably been

added which he had previously overlooked. To most chemists the task which Dr. Bolton has completed would seem an appalling one. To those who know him personally his success will not seem surprising. It is a wonderful book in every respect. Dr. Bolton's interest in this matter is further evidenced by his recent letter to *Science*, printed also in the *Chemical News*, of July 7.

E. H.

SCHOOL CHEMISTRY. BY CHARLES BASKERVILLE, PH.D., The University of North Carolina. Richmond, Va.: B. F. Johnson Publishing Co. 1899. 159 pp. Price, 60 cents.

This book has been prepared for use in high schools, and academies, and is intended to give the pupil an elementary knowledge of the more important chemical facts and theories, especially those connected with every-day life. The book is divided into thirty-seven lessons, each of which consists of a few pages of descriptive text, followed by several well-described and pertinent experiments. Water is first taken up, then atoms, oxygen, air, oxidation, the other non-metals, five lessons on organic chemistry, metals, salts, the soil, vegetable and animal chemistry. The aim of the book is well carried out by the author, but it may be questioned whether the aim of "*school*" chemistry should not be primarily to train and discipline the mind by the use of the scientific method, as well as to interest the pupil in the study of natural science, and only secondarily to impart knowledge of chemical facts and theory. This order is reversed by the author.

The make-up of the book is good, the proof-reading unusually thorough, but the book is marred by many carelessly constructed sentences and loose statements. There is a very complete index.

JAS. LEWIS HOWE.

A SHORT HISTORY OF THE PROGRESS OF SCIENTIFIC CHEMISTRY IN OUR OWN TIMES. BY WILLIAM A. TILDEN. Longmans, Green, and Co., 39 Paternoster Row, London, New York, and Bombay. 1899. ix+276 pp. 12mo.

Dr. Tilden, the well-known professor of chemistry in the Royal College of Science, London, in the spring of 1898, gave a course of lectures to working-men on the progress made in the science and practice of chemistry during the preceding sixty years. Only able to sketch in very broad outline the general features of the subject, he felt the need of some book of moderate size to

which he could refer his hearers, and which would afford a historical survey of the succession of events that led up to the system of theory in chemistry accepted at the present day. Finding no such book he wrote the volume under review. To appreciate the work one must have some knowledge of elementary physics and chemistry, for it does not profess to be a text-book. The period covered by Dr. Tilden, corresponds to the reign of Queen Victoria, and the book might well have been named "Evolution of Chemistry in the Victorian Era." In ten chapters, the author treats of matter and energy; the distribution of the chemical elements and their recognition by the chemist; the rectification and standardization of atomic weights; the numerical relations among the atomic weights and classification of the elements; origin and development of the ideas of valency, and the linking of atoms; the development of synthetical chemistry; the origin of stereochemistry; electricity and chemical affinity; and the liquefaction of gases.

Dr. Tilden writes clearly, has a full acquaintance with his subject, and selects the material judiciously; he is liberal in giving credit to each discoverer for his share of joint work in developing a given theory or law. In writing of the development of certain branches of chemistry he recognizes the work of our own Morley, J. P. Cooke, and F. W. Clarke, as well as that of the French, Russians, Germans, and Italians.

At the close of the volume the author gives a useful list of "Important Events Arranged in Chronological Order;" in this we find the invention of Bunsen's gas-burner credited to the year 1866, but the reviewer is perfectly certain that the "Bunsen-burner" was used in the Heidelberg laboratory many years earlier; it was thought no novelty in 1864.

Dr. Tilden writes in conclusion:

"In the ancient universities of Great Britain . . . . the spirit of mediævalism is no longer wholly predominant. We may therefore look forward hopefully to the day, not far distant, when science and letters, no longer fierce competitors for academic vintage, may walk hand in hand, each conscious of her own dignity, but ready to yield to the other her due share of honor."

The volume successfully carries out the intentions of the

author, and can be recommended to all interested in the development of physical science. HENRY CARRINGTON BOLTON.

EXAMINATION OF WATER CHEMICAL AND BACTERIOLOGICAL. By WILLIAM P. MASON. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1899. 135 pp. Illustrated. Price, $1.25.

This book is divided into three parts: First, an introduction, pointing out the popular misconception of water analysis and emphasizing the necessity of knowing the source of the sample in order to properly interpret the result of the analysis. To this end, throughout the book, much matter is given to enable the analyst to pass upon the quality of a drinking-water from his analysis. Part two gives directions for sampling, and methods of chemical analysis. It is needless to say that these latter, coming from such an authority upon water analysis, as Prof. Mason, are of the best, and are well arranged. Part three deals with so much of the biological examination of water as is of most use to the chemist, leaving the wider field of ultimate differentiation to the biologist. RICHARD K. MEADE.

THE LIQUEFACTION OF GASES. By J. CAURO. Paris: Gauthier-Villars. 1899. 83 pp.

This treatise on the liquefaction of gases has the thoroughness that one might expect if it were prepared for presentation to a class of students specializing in the subject. There is a cryogenic laboratory at Leyden; it is not hard to foresee the establishment of a chair of *cryogenics* at some enterprising university. But everyone at the present moment wants the thermodynamics of gases explained to him. It should be done scientifically, fully, and consecutively. The mathematics involved is anything but abstruse; the facts are entertaining and the story of the successive steps in its history positively fascinating. The work in review could hardly be more fitted to serve for such a purpose as a full scientific presentation of the subject.

The discussion of the physics of gases in the first chapter, of their curves near the critical-point and of isothermals, leads up to the discussion of the Joule-Thomson effect, and closes with a scheme of methods of refrigeration. It is interesting to note amongst these "the principle of cascades." This was the basis of Pictet's work. Another way of expressing it would be by successive falls in the critical-points of the liquids used, one being volatilized to chill the next, and so on until the required

temperature is reached, when a low pressure will be effective for the liquefaction required. Also, the much-discussed application of the Joule-Thomson effect or gain in the circulatory, self-cooling, expansion or sudden-release methods.

In the description of the experimental work of the past, and the practical methods of liquefaction now in use, all the workers in the field seem to have received their just meed of notice, and no signs of dispute about priority are given. A chapter is taken up with historical data, mention of papers, their dates of publication, etc., and the last entry records the communication of Dewar, to the Royal Society, May 10, 1898, reporting the production of liquid hydrogen and helium. In the last chapter are given the applications of liquefied gases, and certain ideas suggestive for chemists are found here such as the preparation of pure oxygen from liquid air, the possible use of liquefaction for separation or analysis of gases, for concentration of solutions, preparation of salts, etc. No thermometric or cryometric methods are mentioned except the mere reference to the use of a hydrogen thermometer by Olzewski. It is a curious sin of omission, as this is now a most promising field of physical research and pertinent to the author's subject. C. F. McKENNA.

ELEMENTARY STUDIES IN CHEMISTRY. By JOSEPH TORREY, JR., Instructor in Harvard Univ. New York: Henry Holt & Co. 12mo. 49 illustrations. viii + 487 pp.

Some years ago during a symposium on the teaching of chemistry Dr. F. W. Clarke remarked that the best method to be pursued depended altogether upon circumstances,—upon the age of the pupils, their previous training, etc. The statement contained a great deal of practical wisdom. Few teachers fail to be profoundly influenced by their environment. If they write textbooks for student use as Professor Torrey has done the nature of this environment becomes at once more or less evident. Professor Torrey has charge of the chemical instruction in the Summer School of Harvard University, and in preparing this book he has evidently had in mind the needs of the class of students who attend such schools—mainly teachers, with inadequate training, bent on self-improvement, willing and anxious to work, mature in years and experience.

The book bears ample evidence of great care in preparation. It is not too much to say of it that it contains one of the most carefully constructed and logical arguments from chemical fact to chemical theory that has ever been written.

In plan the idea is comprehensive. It is to teach the elements of all phases of chemical science. Nothing is shirked, and every point is clearly and sufficiently explained. Each day's work consists of two parts: Laboratory work which comes first and establishes the facts, and the lecture which follows, explains, systematizes, and enlarges on them. While the sequence of treatment is largely in accordance with the periodic law the author by no means binds himself to this order, considering the needs of the student of first importance.

The book contains a few slips in statement of facts, fortunately of small importance, and some infelicities of expression. These will doubtless be remedied in subsequent editions. Every teacher can learn something from Professor Torrey, and all should read his book. E. H.

THE MINERAL INDUSTRY: ITS STATISTICS, TECHNOLOGY AND TRADE IN THE UNITED STATES AND OTHER COUNTRIES TO THE END OF 1898. EDITED BY R. P. ROTHWELL. VOLUME VII. New York and London: The Scientific Publishing Co. 1899. 4to. xxviii+982 pp. Price, $5.00.

To the chemist and technologist the annual volumes of this series are of great interest and value, embodying as they do the latest progress in the different departments of metallurgy and mining. Much of the information is original and cannot be found elsewhere. Among the items of interest contained, it may be noted that the production of aluminum in the United States was 5,200,000 pounds. Ferromolybdenum was produced to the extent of 2,100 pounds, valued nominally at 50 cents per pound. Molybdenum was first produced in the United States to the amount of 9,550 pounds, worth about $1.25 per pound. 33,200 pounds of metallic tungsten, 1,594,152 pounds of carborundum, 3,584,586 barrels of Portland cement of 400 pounds each, 185,647 pounds of artificial graphite, and 8 tons of molybdenite were produced in this year.

The volume contains a vast amount of information, of which it is impossible to give even a digest in the space available. There are articles, for instance, upon the manufacture of con-

centrated alum, asphaltum refining, the hydraulic cement industry, firebrick manufacture, kaolin, the electrolysis and refining of copper, the identification of gems, the technology of gypsum, lime and lime-burning, manufacture of acid phosphate of lime, occurrence and recovery of sodium carbonate in the great basin, manufacture of chamber sulphuric acid, and numerous articles on progress in metallurgy written by specialists.

E. H.

THE RISE AND DEVELOPMENT OF THE LIQUEFACTION OF GASES. By WILLETT L. HARDIN, Ph.D. New York and London: The Macmillan Company. 1899. 244 pp. Price, $1.50.

The recent achievements in the liquefaction of gases, and the very general interest which of late has been manifested in this line of investigation has naturally led to the publication of several works on this subject. One of the best of these is the volume by Dr. Hardin. In the preface the author states that "while the book has been written in a popular-science style, an effort has been made to make it of value to those who are especially interested in the subject by giving the references to the original literature." This latter feature might be adopted with great advantage in all books of a similar nature.

The author devotes about one-third of the volume to an account of the results obtained by the earlier experiments up to about 1860, including the work of Faraday, Thilorier, Natterer, and others. Then follows a chapter on critical constants, the continuity of the gaseous and liquid states of matter, and a statement of the equation of Van der Waals.

The second half of the book is devoted to the liquefaction of the so-called permanent gases, commencing with the methods employed and the results obtained by Cailletet and by Pictet in 1877. A section is devoted to the experiments of Wroblewski and Olszewski, and those of Dewar. Several pages are given to the so-called regenerative method which has been employed by Linde and by Tripler in the liquefaction of air on a large scale. Another section is devoted to the liquefaction of argon and helium, and to the method employed by Dewar in the production of liquid hydrogen in a static condition. A table of physical constants is given, and in conclusion the author discusses briefly the three states of matter, some of the applications of liquefied

gases, and the effect of low temperatures upon physiological action. The volume is a clear, well considered, and reasonably full statement of our present knowledge on the liquefaction of gases.

E. G. LOVE.

QUALITATIVE ANALYSIS FOR SECONDARY SCHOOLS. By CYRUS W. IRISH, A.B. New York: American Book Company. 100 pp.

The usual college course in qualitative analysis is simplified by omitting oxalates and phosphates, and determinations other than spectroscopic for sodium and potassium. The test for chromium is made more striking by oxidation with hydrogen dioxide and subsequent precipitation as lead chromate; the alternative method by fusion is also given. Preliminary experiments on bases are the customary ones, all bearing directly on qualitative separations, but they hardly carry out the author's prefatory claim of a study of descriptive chemistry of bases by laboratory methods. A praiseworthy effort is made to keep alive the student's interest in general descriptive chemistry by a considerable number of questions on that subject. Questions are put also on the experiments performed. Uniformly these call into play only the student's power of observation, and it would seem well to ask some questions beginning with "why"; questions to bring out reasons for steps taken. Observations of the form of precipitate, whether flocculent, crystalline, etc., are omitted. Likewise omitted, are directions for careful manipulation. An unsatisfactory condition of mind and knowledge must result from this statement regarding the solubility of freshly precipitated zinc sulphide in hydrochloric acid: "To confirm the presence of Zn add conc. HCl, when ZnS, if present, will be dissolved, but S in suspension will not dissolve. A partial solution, on addition of conc. HCl, also indicates ZnS." This should be a satisfactory manual in the hands of a good teacher. It will not compel good teaching.

H. M. ULLMANN.

THE ELEMENTS OF BLOWPIPE ANALYSIS. By FREDERICK HUTTON GETMAN, F.C.S. New York: The Macmillan Company. 1899. Small 12mo. 77 pp. Price, 60 cents.

The book begins with cuts of blowpipe apparatus, poorly executed, some important ones omitted, while that of the blowpipe itself shows an antiquated form very seldom used.

Chapter I describes in a fragmentary manner the common apparatus and reagents, omitting some of the most useful. The recommendation to use for blowpiping a Bunsen flame one centimeter high with air supply cut off, is unfortunate. Half a dozen other devices are better.

Chapter II gives a general outline of blowpipe analysis, following the six primary tests of Berzelius. Here, several of the most valuable blowpipe tests, such as examination in an open glass tube, are omitted altogether. The tests given are only partially described, many details necessary for successful practice being omitted.

Chapter III, giving reactions for the detection of the elements, arranged alphabetically, is very unsatisfactory. The reactions given are, in general, those of the oxides only, and misstatements are numerous. Chapter IV, giving the behavior of some of the principal metallic ores, is little better.

There are in the book at least a score of downright misstatements, and another score which are inaccurate because of their incompleteness. The omissions are startling,—gold, selenium, tellurium, molybdenum, titanium, tungsten, uranium, and vanadium not being even mentioned in any connection.

What is correct in the book is well expressed, and the type is clear, but the book as a whole does not deserve a place in blowpipe literature.

JOSEPH W. RICHARDS.

A TREATISE ON THE KINETIC THEORY OF GASES. By S. H. BURBURY, M.A., F.R.S. J. and C. F. Clay at the University Press, Cambridge. New York: The Macmillan Company. 1899. vii + 157 pp. Price, eight shillings.

The object of this book as expressed by the author is to apply to the kinetic theory of gases a method of analysis different from that generally employed. Previous writers have always started with the fundamental assumption that with regard to their relative motion the molecules of a gas are independent of one another. To express this independence the law of distribution of momenta assumes the form E^{-hQ}, and the expression relating to the translation velocities becomes, $Q = \Sigma m(u^2 + v^2 + w^2)$, m being the mass and u, v, and w the component velocities. Boltzmann deduces his H theorem and the theorem of the equality of

mean kinetic energy for each degree of freedom from the above-mentioned independence and from the form of Q given. The author gives to Q the form $Q = \Sigma m (u^2 + v^2 + w^2) + \Sigma\Sigma b (uu' + vv' + ww')$, where b is a negative function of the distance r at the instant considered between the two molecules whose velocities are u, u', etc., which function is inappreciable except for very small values of r. The author shows that without the coefficient b the motion can not be stationary. Other investigators have proved that assuming the independence, the motion is stationary; the author does not question the proof but the axiom. The result of giving to Q the new value is that molecules near to each other have on an average a motion in the same direction; *i. e.*, they tend to form streams. The author admits that the usual form holds very well for ordinary gases under ordinary conditions, since for them the b coefficients are probably very small, but he maintains that his form is more general, applying without restriction as to density, except when the gas is liquefied or very near its point of liquefaction.

The subject is treated in ten chapters to which is added a short appendix containing proofs of certain mathematical propositions (relating chiefly to determinants) used in the book. Throughout the work the author considers critically the methods and results of other prominent writers on the kinetic theory in connection with his own. The style is clear and forcible. The book is not a treatise that seeks to present the subject in an elementary form; it is rather a piece of original work which every student of the kinetic theory should read.

The book is printed on good paper. The type is clear and the cloth binding is neat and durable.

The appearance of this book is additional evidence that interest in the kinetic theory is still being maintained in spite of the fact that kinetic explanations are at present viewed rather with disfavor by a number of prominent scientists.

LOUIS KAHLENBERG.

INORGANIC CHEMICAL PREPARATIONS. By FELIX LENGFELD, Assistant Professor of Inorganic Chemistry in the University of Chicago. The Macmillan Company. 1899. 57 pp.

The teaching of inorganic chemistry in the laboratory has been developed along analytical lines almost entirely. While there is

getting to be a livelier appreciation of the value of the synthetical chemistry as a part of every chemist's training, there is even now a comparatively small number of laboratories where a regular course in the preparation of pure inorganic compounds from crude and impure materials, is required of the students. Wherever such a course is offered, or contemplated this little book of Dr. Lengfeld's will be welcomed. It contains careful and *workable* directions for the preparation of about fifty compounds, beginning with easily prepared substances, like sodium chloride, potassium chlorate, and acid sodium carbonate, and proceeding with compounds the preparation of which requires greater experience and skill, and finally ending with hydrogen dioxide, hydroxylamine sulphate, and phosphonium iodide.

To quote from the preface: "An attempt has been made to introduce all processes generally used, and at the same time to avoid repetition. The student should study each preparation in detail, work out other methods of making the same substance, understand and criticise every step he takes and read some original articles. Therefore references to the literature have been given." The student who conscientiously follows this advice, and works through such a list of preparations, will find his knowledge of chemistry increased quite as much as it would be by any equal amount of labor that he could undertake.

G. M. RICHARDSON.

THE ELEMENTS OF QUALITATIVE ANALYSIS. By WM. A. NOYES, PH.D., Professor of Chemistry in the Rose Polytechnic Institute. Fourth Edition. Henry Holt & Co. 1897. 97 pp. Price, 88 cents.

Each one of the earlier editions of this work has proved itself an extremely useful and complete outline of the general subject covered by Fresenius in his larger work on Qualitative Analysis. The present edition does not differ radically from those preceding it, but it embodies many useful additions and minor changes, which will increase its value. Its mode of treatment throughout is characterized by the same explicitness in the directions to students. Copious tables of reactions are a feature of the book. A brief introductory chapter upon the dissociation theory of solutions calls attention to the many applications of the theory

and emphasizes the importance which it seems likely to take in the near future in the teaching of analytical chemistry.

F. C. PHILLIPS.

THE COMPENDIOUS MANUAL OF QUALITATIVE CHEMICAL ANALYSIS OF C. W. ELIOT AND F. H. STORER, AS REVISED BY W. R. NICHOLS. By W. B. LINDSAY, Professor of General and Analytical Chemistry in Dickinson College, and F. H. STORER, Professor of Agricultural Chemistry in Harvard University. Nineteenth Edition, Newly Revised. New York: D. Van Nostrand Company. 1899. vii+202 pp. Price, $1.25 net.

The publication of nineteen editions in thirty years of a scientific book is ample evidence both of the value of the work and of the general appreciation of its value. This is particularly true of a work of this kind when every teacher of qualitative chemistry seems to find it necessary to publish a book covering this course for the special benefit of the pupils in the institution to which he is attached.

The plan of the work is excellent and follows the course which should be pursued by any one beginning the study of qualitative analysis. Beginning with examples of the separation of two elements, the student is led gradually on to the separation of the groups and the different members of each group. The treatment of an unknown substance follows, and so through the entire range of the subject. The descriptions are uncommonly clear and the language is simple and vigorous. The changes from the first revised edition are very slight and are in line of improvement, but some of the old cuts of apparatus are antiquated and below the standard of the rest of the book.

ANDREW A. BLAIR.

BOOKS RECEIVED.

The Compendious Manual of Qualitative Chemical Analysis of C. W. Eliot and F. H. Storer, as revised by W. R. Nichols. Nineteenth edition, newly revised by W. B. Lindsay and F. H. Storer. New York: D. Van-Nostrand Co. 1899. vii+202 pp. Price $1.25 net.

Wheat. Bulletin No. 83. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. August, 1899. 20 pp.

The Elements of Blowpipe Analysis. By Frederick Hutton Getman, New York: The Macmillan Co. 1899. x + 77 pp. Price, 60 cents.

The Chemical Composition of American Food Materials. By W. O. At-

water and A. P. Bryant. Bulletin No. 28. (Revised edition.) Washington: U. S. Department of Agriculture. 1899. 87 pp.

Description of a New Respiration Calorimeter and Experiments on the Conservation of Energy in the Human Body. By W. O. Atwater and E. B. Rosa. Bulletin No. 63. U. S. Department of Agriculture. 1899. 94 pp.

Studies on Bread and Bread Making. By Harry Snyder and L. A. Voorhees. Bulletin No. 67. U. S. Department of Agriculture, Washington, D. C. 1899. 51 pp.

A Course in Quantitative Chemical Analysis, Gravimetric and Volumetric. By Nicholas Knight, A.M., Ph.D. New York: A. S. Barnes & Co. 1899. x+110 pp. Price, 80 cents.

Indicators and Test-papers: Their Source, Preparation, Application, and Tests for Sensitiveness. By Alfred I. Cohn, Ph.G. New York: John Wiley & Sons. 1899. ix+249 pp. Price, $2.00.